Wastewater and Biosolids Management

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Contents

Preface

The irrigation water shortage is becoming more acute in many regions of the world, where the 'irrigation agriculture' is the basic source of food production. The water scarcity due to the xerothermic conditions and to climatic changes occurring in these regions, is a serious problem. The effort to find alternative irrigation water sources is included among the basic priorities of many state officials.

It is true that since the ancient times, wastewater has been used extensively for agricultural production. In fact, at ancient times, this practice was the most environmentally friendly.

However, not only in antiquity, but also in contemporary times, wastewater reuse is considered an attractive option for the recycling of marginal fresh water while partially covering the needs for irrigation water used forcrop production. Unfortunately, modern technological era has decreased significantly the level of environmental friendliness of wastewater reuse in agriculture. This is due to the toxic substances contained in wastewater, which are being spread in the environment and in the food chain via plant uptake. As a result of wastewater reuse, toxic metals and organic compounds, pharmaceutical products, xenobiotics, microplastics, agricultural chemicals, and other micropollutants are spread in the environment, rendering wastewater reuse less friendly. The existence of so many macro and micropollutants in the aquatic and terrestrial systems has been a great puzzle for the contemporary humans. Large sums of money are spent to improve wastewater quality so as to make it more safe and friendly to the environment.

The relevant research work that has been conducted during the last 40 years, in many countries, aims at studying the various aspects of wastewater reuse such as the improvement of the processing technologies, the quality of the wastewater treatment plant effluents and theproduction of treated wastewater as safe and healthy as possible. Furthermore, recent research is focusing on tackling the control of micropollutants in aquatic and terrestrial systemssince their presence jeopardizes the environmental quality and constitutes a potential threat for human and animal health. Novel technologies are being developed for wastewater management in response to the changing regulatory requirements and with the view to attain safe reuse and to protect as effectively as possible human health and the environment. As it is pointed by various researchers, safe reuse will be accomplished by applying a "science-based" wastewater and sludge reuse. This is possible only if it is based on new research findings and on the reconsideration of the official guidelines, which are currently being used.

The aim of this book is to present the recent developments on aspects of wastewaters and sludge reuse and more specifically on the following subjects:

- Wastewater management in ancient times
- Wastewater management and new technologies
- Biological processes of nutrient removal and energy recovery
- Nanofiltration and energy cosumption
- Removal of pharmaceuticals and personal care products in costructed wetland from wastewater management
- Heavy metal interactions under the effect of the wastewater
- Microplastics and synthetic fibers in treated wastewater and sludge
- Wastewater reuse: Uptake of contaminants of emerging concern by crops
- Advanced oxidation processes for wastewater treatment
- Bio solids composting and soil applications
- Anaerobic digestion and energy recovery from wastewater sludge
- Existence of organic micropollutants in the environment due to the wastewater reuse and biosolids application

The present publication is made within the context of the International Water Association to keep informed its members and all those involved in wastewater reuse, and biosolid application, on the above developments so as to accomplish safe and effective reuse of these inputs, minimizing health risks and protecting environmental quality.

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Chapter 1

Wastewater management in ancient times

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1.1 INTRODUCTION

Wastewater management, in ancient civilization is a key theme for the development of technologies adapted to a specific area, especially where patrimonial landscape is considered as the determining factor for today's cultural and socioeconomic life (Fardin *et al.* 2013). When considering wastewater management, what emerges is a long history associated with urban ecology and disposal of wastewater enmeshed with societal and cultural traditions (Lofrano & Brown, 2010). According to the principle "the solution to pollution is dilution", dispersion has been the dominant strategy for wastewater management through the ages, but not the solution for protection of the environment and public health. Unfortunately, that policy continues to be practiced in many developing countries to this day (Lofrano *et al.* 2008; Libralato *et al.* 2009; Lofrano *et al.* 2015). Modern humans dwelled on earth for over 200,000 years, most of that time as hunter-gatherers, and with ever increasing populations (Vuorinen, 2007, 2010). The first human communities were scattered over wide areas and waste produced by them was returned to land and decomposed using natural cycles. It was only during the last 9000 to 10,000 years they discovered how to grow agricultural crops and tame animals. This was a new era probably started in the hills to the north of Mesopotamia. From there, the agricultural revolution spread to south Hellas, Sicily, and to the rest of Europe and of course to the east (e.g. Indus Valley) (Angelakis & Zheng, 2015). Because of these changes, there was a greater production of waste and waste products and thus, ecological impacts.

Until the birth of the first advanced civilization, disposal of human excreta was managed through holes in the ground, covered after use as explained by the Mosaic Law of Sanitation (Deuteronomy, Chapter 23). But as society advanced so had the concept of waste management, for example, there is evidence that the oldest known wastewater drainage was in the Neolithic Age (*ca.* 10,000–3000 BC) around 6500 BC in El Kowm (or Al Kawm), located between the Euphrates River and the city of Palmyra in Syria (Cauvin *et al.* 1990). However, that was an exception and most civilizations had no systems of waste disposal. Because of the lack of any kind of records, it is practically impossible to evaluate the health impact of these disposal practices on ancient populations. It is, however, quite safe to conclude that urban centres had serious public health problems due to a lack of management of their wastewater (Vuorinen, 2007; Larsen, 2008).

The self-depurative capacity of water bodies enabled tolerating the discharge of wastewater directly to bodies of water and, as an industrial society developed, industrial wastes as well. Nowadays, water bodies are protected preventing further degradation of their environmental quality since there is a greater understanding of how the self-depurative capacity was compromised by prolonged massive discharges, as, for example, in the case of the River Thames (London, UK) (Halliday, 1999; Arienzo *et al.* 2001; Vita-Finzi, 2012). The complex network of interactions that binds surface water and groundwater suggests that poor river quality can affect human health and the environment due to the presence of substances and microorganisms with potentially (eco-)toxic effects, thereby leading to the loss of biodiversity and impacting human health (Motta *et al.* 2008; Montuori *et al.* 2012; Albanese *et al.* 2013).

Although the importance of proper sanitation for the protection of public health was not understood by modern cities until the 19th century (Brown, 2005; Vuorinen *et al.* 2007; Cooper, 2007), many ancient civilizations did realize the implications of poor wastewater management and did provide some management especially for manure disposal. It is well documented that most of the technological developments relevant to the conveyance of wastewater are not the achievements of present-day engineers, but date more than five thousand years ago to the prehistoric world (Angelakis & Zheng, 2015). Unfortunately, discussions about sewers and primitive treatment is omitted from archaeology and historical research and, thus, forgotten. Now it is important to recover that information from the past to ensure a sustainable future. Therefore, the aim of this chapter is to reveal and describe cultural heritage in various regions of the world, and give a clear understanding of their wastewater management, which contributed to the development of the existing treatment technologies. This chapter has been organized according to the four main geographical areas associated with ancient civilisations: Middle East and India, China, Africa, and the Mediterranean. It is important to note that in the ancient world, wastewater was not separated from stormwater or rainwater drainage so the term "wastewater" used in this chapter includes stormwater/rainwater drainage combined with sanitary waste.

1.2 MIDDLE EAST AND INDIA

Historical records show that the Mesopotamian Empire (3500–2500 BC) was the first civilization to formally address sanitation problems arising from community living. In the ruins of Ur and Babylonia, there are remains of homes which were connected to a drainage system to carry away wastes (Jones, 1967) as well as latrines leading to cesspits. Unfortunately, although this sophisticated system existed, most people in Babylon did not have access to this system and threw debris including garbage and excrement on to the unpaved streets which were periodically covered with clay, eventually raising the street levels to the extent that stairs had to be built down into houses (Cooper, 2007). In some of the larger homes of Babylon, people squatted over an opening in the floor of a small interior room. The wastes fell through the opening into a perforated cesspool located under the house. Those cesspools were often made of baked perforated clay rings, ranging in size from 45 to 70 cm in diameter, stacked atop each other. Smaller homes often had smaller cesspools (45 cm diameter); larger homes had larger diameter cesspools (Schladweiler, 2002). Other great civilizations such as the Minoans and an unknown civilization located on modern-day Crete and the Indus valley respectively, flourished during the Bronze Age (approximately, 3200–1200 BC).

The Indus Valley was also far advanced in wastewater management; having a sophisticated and technologically advanced urban culture (Pathak, 2001). Even as early as 2500 BCE, the region of Harappa and Mohenjo-Daro included the world's first urban sanitation systems as did the recently discovered region of Rakhigarhi (Webester, 1962). The Indus civilizations implemented a complex and centralized wastewater management system, including lavatories, and drainage and sewerage systems (Jansen, 1989; Kenoyer, 1991). The channels were either excavated into the ground or constructed above ground of burnt brick (see Figures 1.1 and 1.2).

However the practice of "open squatting" was frowned upon (Avvannavar & Mani, 2008) and only a few houses had toilet facilities. These toilets were of two types: made of earthenware bricks with a seat; or a simple hole in the floor. The domestic outlet, from toilets and bath platforms, was connected to street drains through a pipe network, or to soak-pits (Jansen, 1989; Wright, 2010), probably which were thereafter dumped in a specific place, as it has been hypothesized for solid waste (Jansen, 1989). Wastewater was not permitted to flow directly to the street sewers without first undergoing some treatment. In this system, wastewater passed through tapered terra-cotta pipes into a small sump. Solids settled and accumulated in the sump, while the liquids overflowed into drainage canals in the street when the sump was about 75% full. The drainage canals could be covered by bricks and cut stones, which likely were removed during maintenance and cleaning activities (Wolfe, 1999), most likely was the first attempt at treatment on record. Canals were built with the necessary slope to transport the water into the river Indus (Wiessmann *et al.* 2007). Following the Harappa model, in Jorwe, in present day Maharashtra, the drainage system was implemented from 1375–1050 BC (Kirk, 1975). In the

3rd century BC at Taxila, domestic wastewater was canalized out from the houses through earthenware drainpipes into soak-pits (Singh, 2008). In the antique Delhi, during the 3rd century BC, the same kind of system was used: drains, which are still visible in todays Purana Qila, canalized wastewater into 'wells, which may have functioned as soak-pits' (Singh, 2006). Later (around 500 BC), Ujjain's 'drainage system included soak-pits built of pottery-ring or pierced pots (Kirk, 1975).

Figure 1.1 Picture of Mohenjo-Daro excavated sewer channel (Hodge, 1992).

Figure 1.2 Picture of Harappan above ground sewer channel constructed of burnt brick (Kirby *et al.* 1956).

1.3 CHINA

China has a long history of drainage, river management, irrigation, urban water supply, and wastewater management: the earliest dates back to around 2000 BC. According to the archaeological discovery, by 2300 BC, urban drainage facilities had been built in various cities. Earliest drainage facilities were discovered in the old town Pingliangtai of the Henan province, where drainage pottery was used. Also, an earthen pipeline for drainage was found for underground drainage system under the streets (HICR, 1983). During the Shan Dynasty (15–10 BC), urban development in China was advanced to a golden age. Many large cities were formed near the Yellow River basin and urban drainage improved accordingly. Archaeological discoveries from Yanshixihaocheng which is todays Yan Shi city of the Henan province, had an efficient drainage system that was built inside the city. According to archaeologists, the city had an area of 1.9 million m^2. The underground 800 m main urban drainage raceway from the East Gate to the palace formed a well-designed drainage system and included down-spouts for drainage of rainwater and wastewater from the palace itself. The underground raceway was 1.3 m in width and 1.4 m high, draining water from the palace and town into the City River (HICR, 1983).

1.4 AFRICA

Egyptians also employed sanitation practices. According to the description of Herodotus (Histories II), finer houses in the city of Herakopolis (BC, 2100), had bathrooms with toilets seats made of limestone. The bathroom would be fitted with a slightly inclined stone-slab floor and the walls were typically lined to a certain height (about half a meter) with battered stone slabs to protect against dampness and splashing (Breasted, 1906). Drainage of wastewater was provided by setting a basin beneath the spout of the floor slab in the bathroom, or sometimes by drainage channels running through the outer wall into a vessel or straight into the desert sand. The less wealthy, who could not afford to have a limestone toilet, used toilet stools with holes in the middle under which a ceramic bowl was placed. Additionally, toilet stools with a clay pot beneath were also used as portable toilets and were often buried with senior officials (Breasted, 1906). The contacts of Minoans with Egypt intensified from the period of the first palaces (*ca*. 1900–1700 BC). Therefore, this suggests that a possible influx of technology related to water, wastewater, and stormwater management in this particular era should be in existence (Angelakis & Zheng, 2015). This assumption is based on the similarities of hydro-technologies developed by Mesopotamian, Egyptian, Minoan, and Indus valley civilizations.

1.5 MEDITERRANEAN AREA

The Greeks were forerunners of modern sanitation systems Golfinopoulos *et al.* (2016). Archaeological studies have established unequivocally that, the origin of modern technologies of water management dates back to ancient Greece. From the early Minoan period (*ca*. 3200–2300 BC) issues related to sanitary techniques were considered of great importance and developed accordingly. Archaeological and other evidence indicate that during the Bronze Age advanced wastewater and stormwater management were practiced (De Feo *et al*. 2014). The status of urban sewage and stormwater drainage systems in ancient Greece is well documented by Angelakis and co-workers (2005, 2007). They reported that toilets similar to Egyptian ones were found at the Palace of Minos in Knossos and in the west side of the so called "Queen's apartment" at Phaistos. They were connected to a closed sewer, which still exists and is working after 4000 years (Angelakis *et al*. 2005) (Figure 1.3). Angelakis and Spyridakis (1996) provide a detailed description of the sewage system of Knossos which exceeds one hundred and fifty meters. Some of the sewers were large enough for people to walk through. Many of the drains from *ca*. 2000 BC are still in beneficial service today on Crete.

Figure 1.3 Parts of the sanitary and storm sewage systems of Knossos Palace (Lofrano & Brown, 2010).

As the Minoans, Egyptians, and Indus valley civilization developed trade relations with the Greek mainland, they influenced the Myceneans (ca. 1600–1100 BC) and Etruscans (ca. 800–100 BC) in the west and ancient Indian, and the Chinese in the east. The Myceneans and Etruscans were the most direct ancestors of the later Hellenes. Thereafter, the cultural diffusion that resulted from trade contacts with the Hittite Empire and Egypt began to deteriorate. The Etruscan civilization built some of the first organized cities in central Italy around 600 BC (Scullard, 1967). Marzobotto, one of the more important Etruscan cities, had a skilfully designed drainage system making use of the natural slope to keep the city dry and clean. In addition, paved streets and stepping-stones in the roadways acted as protection for pedestrians against stormwater runoff (Strong, 1968). The Etruscans, similar to other ancient civilizations, formed the perspective of urban runoff as a nuisance flooding concern, a waste conveyor, and a vital resource.

Unforutnately, all these remarkable civilizations collapsed even with their advanced capabilities in providing water supply. The interesting question is whether or not water resources sustainability was a significant component for their failure (Mays *et al.* 2007) or prevented failure from happening earlier.

Advanced techniques were also developed in the Aegean islands during the Cycladic period (ca. 3100–1600 BC). The archaeological investigation of the island of Thera (also known as Santorini), in the Cyclades island complex, found at least five terracotta bathtubs. All of them must most likely, were in use until the great eruption of the Thera volcano around 1600 BC. They were found in several places during the excavations; one was in a room that must have been a bathroom, equipped with an advanced sewage system (Koutsoyiannis *et al.* 2008).

Later in the Archaic (ca. 750–480 BC) and Classical (ca. 480–336 BC) periods, both historical sources and archaeological excavations provide evidences that water and wastewater technologies were advanced and widespread in Hellas. Ancient Greeks had public latrines, which drained into pipes, which conveyed wastewater and stormwater to a collection basin outside the city. From there, brick-lined conduits conveyed wastewater to agricultural fields where it was used for irrigation and to fertilise crops and orchards.

Based on archaeological information, the design of the piping system allowed wastewater to flow in one set of pipes from the building to a larger canal in the road, which in turn flowed to a larger main canal and then into a single collector (Tolle-Kastenbein, 2005). A system like this was found between the Acropolis and the hill of the Pnyx where archaeologists have unearthed a series of canals converging in a single collector. Of course not all the villages needed this complex series of pipes and canals, but they were certainly present in cities like Athens, Thasos, Pergamum and Pompeii and perhaps many other cities that have not yet been studied.

The Romans were brilliant managers and engineers and their systems rivalled modern technology. Rome's water system is one of the marvels of the ancient world. Much is known and has been written about Rome's water supply (Hodge, 2002; Cooper, 2007). Much less has been said of the impact wastewater management had on the Roman lifestyle. Although sewer and water pipes were not inventions of the Romans, since they were already present in other Eastern civilizations, they were certainly perfected by the Romans. The Romans resumed the engineering works of the Assyrians, and turned their concepts into major infrastructure to serve all the citizens of the Roman Empire.

Inventors of the first integrated water service, the Romans managed the water cycle from collection to disposal, providing dual networks to collect spring water and dispose of storm and wastewater. Romans realised that spring water had much better quality for human consumption than that derived from surface water bodies, but they also realized that surface water could be used for other activities. Furthermore, they recycled wastewater from the spas using it to flush latrines before discharging the waste into sewers and then into the Tiber River (Jones, 1967). Although the rich had their own baths and toilets, the majority of Romans lived in tenement houses (*Insulae*). Unfortunately, these people usually disposed of trash by throwing it out of windows, a practice that would be followed until the Middle Ages. Therefore inhabitants of poor neighbourhoods were continually exposed to epidemics.

In an attempt to improve such conditions, latrines, public baths, and water fountains were made available to even the poorest citizens (Vuorinen, 2010). Public latrines were discovered in Ostia (Rome, Italy) and in Ephesus, Turkey. In addition to the famous aqueducts for supply of fresh water, ancient Rome had an impressive sewage system. The most famous as well the largest known ancient sewer is the Cloaca Maxima. It was built under the dynasty of Tarquin (VI century BC), nearly three centuries before the first aqueduct (Aqua Appia 312 BC). Initially constructed to drain the marsh for the eventual building of Rome, it originally stretched more than 100 m through the centre of the *Forum Romanum*, between the later *Basilicae Aemilia* and *Julia*. It was built so solidly and with such foresight that the Romans used it for over 2500 years and a section close to the "Torre dei Conti" is still working today. Within decades of completing this monument, Romans added smaller canals to drain nearby areas and began extending the main duct to the *Velabrum*. In the following centuries, repairs, extensions, additions and renovations changed the architecture and course of the canal. The most famous manhole of cloaca, known as the "Mouth of truth". The Cloaca Maxima spread throughout the city-center; new shafts drained each of the imperial fora, the area around the Carcer, Temples of Saturn and Castor, and included a large duct running alongside the Via Sacra and all fed into the main channel in front of the Basilica Aemilia. To the south, the Cloaca Circi Maximi originally drained the area of the Circus Maximus, but later connected to drainage systems for the Coliseum and perhaps the area of the Baths of Caracalla (Lanciani, 1897).

Traces of Roman Canals were found in all major cities of the empire and show a variety of engineering and construction techniques, which were used depending on the geology of slopes and the distance to the receiving water body. Different designs were adopted in the territory of ancient *Pompeii* and *Herculaneum*. Cesspools were the most frequent solution attempted to manage wastewater in Pompei, which extended over porous lava layers, able to easily absorb rain, urine and faeces. Cesspools were also used in Herculaneum, although much less frequently and were located on sites with steeper slopes and a compact subsoil of volcanic tuff (Sori *et al.* 2001). The end of the Roman Empire led to the deterioration of the aqueducts and sanitation systems.

1.6 CONCLUSIONS

Although there are differences in the technology used today and the scale of applications, there are no differences in the fundamental principles used for wastewater management; convey, treat, and dispose. The durability of some of the ancient systems, some of which operated until present times, as well as scientific and engineering principals and the transfer of that information enabled ancient wastewater management to be inherited by future societies. Many of these ancient societies understood the importance of wastewater management to protect human health and the environment. However, for many years that understanding was lost. When the Roman Empire collapsed, the sanitary dark ages began and lasted for over a thousand years (476–1800) (Lofrano & Brown, 2010). People would toss waste into the streets, wastewater would run in open trenches along the walkways, and chamber pots would be emptied out of windows. During that period, epidemics raged through the majority of European cities. Waste leached into the ground water and contaminated wells. Rivers in London and Paris were open sewers. In the early 20th century, developed countries introduced wastewater treatment and separation of wastewater from stormwater and rainwater, but there are still many developing countries that are in the sanitary dark ages. Some societies do not even have primative toilets. The ancient cultures discussed in this chapter had more sophisticated waste management and complex drainage systems that some developing countries have in the 21st century.

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Chapter 2

Wastewater management: introduction to new technologies

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The major driving force for developing new technologies for wastewater management is simply population increase, which however is coupled with rising global standards of living and climate change (Daigger, 2008). New technology creates interest in the municipal wastewater treatment field because it serves a new or an existing need in a creative manner and is therefore deemed innovative. Actually, the definition of new technology is synonymous with technological innovation. Innovative wastewater treatment technologies are developed to respond to changing regulatory requirements, increase efficiency, and enhance sustainability or reduce capital or operating costs (Parker, 2011).

Water use has been growing at more than twice the rate of population increase in the last century. Water stress currently affects only a modest fraction of the human population, but it is expected to affect 45 percent of the population by 2025. Around 1.2 billion people, or almost one-fifth of the world's population, live in areas of physical scarcity, and 500 million people are approaching this situation. Another 1.6 billion people, or almost one quarter of the world's population, face economic water shortage (where countries lack the necessary infrastructure to take water from rivers and aquifers). This situation will be further exacerbated by global climate change, which is altering water-supply and storage patterns in ways that make existing water management infrastructure less effective (WRI, 1996).

The increase in the amount of nutrients, especially nitrogen and phosphorus, in the aquatic environment, is another aspect of water stress caused by urban water management systems (Steen, 1998; Wilsenach *et al.* 2003). Phosphorus, which is mined as phosphate rock, and nitrogen are used as fertilizers. Phosphorus and nitrogen then pass through us, as we metabolize food, and end up in the wastewater stream. When these effluents are discharged to the aquatic environment, the excess nutrients can cause eutrophication. At the current rate of consumption, the supply of phosphate, an essential nutrient with no known replacement, is expected to be exhausted in about 100 years. Thus, removal/recovery of nitrogen and especially recovery of phosphate from the wastewater streams is more than necessary.

Sludge production, management and final disposal still remains an unsolved problem even in developed societies. Sludge, which is a mixture of organic and inorganic substances, contains remaining organic carbon, nutrients, non-biodegradable compounds, heavy metals and pathogens. Even though its usable forms have been greatly promoted, existing technologies cannot alleviate the impact of this controversial material. In addition, the quantities of produced sludge steadily increase causing serious problems, especially to developing countries.

After several decades of operation of the conventional wastewater treatment plants, new issues arise concerning novel technologies and new data, demanding the adaptation of new strategies and more effective and economical solutions. The need for new approaches to urban water and resource management is also being driven by the need for sustainability, which includes social, environmental, and economic goals (Daigger & Crawford, 2005). Sustainability also requires to reduce energy consumption and operating costs and to make treatment plants more efficient. The challenge is to develop and implement approaches to urban water and resource management, and the supporting technologies to meet these goals.

This chapter focuses on the new applicable technologies, which aim to adapt wastewater treatment to the new environmental, economic and social data and promote sustainability. Innovative nitrogen removal, phosphorous recovery, membrane bioreactors, advanced oxidation processes, sludge treatment and disposal are the issues addressed in what follows. Most of these technologies will be discussed in detail in the following chapters.

2.1 CLIMATE CHANGE EFFECTS ON WASTEWATER TREATMENT

Due to increasing concentrations of greenhouse gases in the atmosphere, temperature is expected to rise between 2 and 5°C globally by 2050 (Zouboulis & Tolkou, 2015). This temperature increase already causes, among others, increased evaporation rates, more extreme weather events (floods, droughts, hurricanes, etc.), earlier snow melt and reduced precipitation (heavier but less frequent in some areas). As a result of more common flooding events, by-pass becomes a frequent operating procedure for wastewater treatment plants (WWTPs), which receive wastes from combined (urban waste and storm water) sewage systems. This means that in order to protect the biomass in the aeration basin and avoid biomass washout, the incoming wastewater with the storm-water are diverted directly without any treatment to the closer water recipient.

Also, temperature increase affects drastically dissolved oxygen solubility. Oxygen solubility in water is reduced from 9.15 mg/L at 20°C, to 8.63 mg/L and

7.87 mg/L at 23°C and 28°C, respectively. Thus, extended aeration will become a prerequisite. In addition, minor temperature changes can have significant effects on biological reactions. The temperature effect on biological growth is described by a typical Arrhenius-type expression:

$$k = k_{20} \cdot \theta^{T-20}$$

where k is the reaction rate constant at temperature T, k_{20} is the reaction rate constant at 20°C, θ is a temperature coefficient (dimensionless), and T is the temperature of the biological reactio. The reaction rate constant k, takes the value of 0.1 d^{-1} for a sample of BOD (300 mg/L) at 20°C (k_{20}). The current value is $k_{23} = 0.123$ d^{-1}, and it will be increased to 0.142 d^{-1} and 0.174 d^{-1} for a temperature increase of 2°C and 5°C, respectively. Particularly, nitrification which is the slowest aerobic biological process would be seriously affected. As a result of reduced oxygen solubility and increased biomass growth the design of new WWTPs and the operating procedure of existing ones should be reconsidered.

On the other hand, many gases evolve from wastewater treatment plants that contribute to the greenhouse effect. Organic carbon oxidation produces new biomass and CO_2. Anaerobic digestion produces biogas which contains about 60–70% CH_4 and CO_2. Finally, denitrification converts nitrite to gaseous forms of nitrogen (e.g. N_2O, N_2) that are becoming more prevalent as the industry moves toward complete nutrient removal. Compared to the same mass of CO_2 released in the atmosphere, CH_4 has 21 times and N_2O has 310 times as much global warming impact. CH_4 and N_2O represent about 3.6 percent of the total greenhouse gas (GHG) emissions on a CO_2 equivalent basis (EPA, 2009). From this 3.6 percent, 0.6 percent is due to wastewater treatment. As climate change is a major concern, alternatives should reduce both greenhouse gas emissions and power consumption, making anaerobic treatment a more attractive component of novel approaches to treatment processes.

2.2 INNOVATIVE NITROGEN REMOVAL

Activated sludge systems have been successfully used initially for carbon and later for nitrogen and phosphorous removal for almost a century. The growing public concern for environmental protection has led to the implementation of continuously stricter effluent standards. Ammonia removal is of great concern since nitrogen is one of the main contributors of eutrophication. For this purpose, ammonia is converted initially to nitrite and then to nitrate through an aerobic-autotrophic process known as nitrification. The reverse process, denitrification, converts nitrate to nitrite and then to a gaseous form of nitrogen (N_2O, N_2) through an anoxic-heterotrophic process. Obviously the intermediate stage of nitrate increases energy consumption, BOD requirement and reactor volume. Several technologies have been developed and applied worldwide to overcome this problem and make nitrogen removal more cost-effective, among them: SHARON- a simple system for N-removal over nitrite, ANAMMOX- ANaerobic AMMonium Oxidation, fully autotrophic N-removal, CANON- combination of nitritation and anaerobic ammonia oxidation (Anammox) and BABE- bioaugmentation with endogenous nitrifiers (IWA, 2008).

SHARON (Stable High Rate Ammonia Removal Over Nitrite) is a cost-effective treatment system for complete removal of nitrogen from wastewater. The system is used for treatment of high strength ammonia liquors. A typical application involves the treatment of liquors from dewatered digested primary sludge and waste activated biosolids at municipal wastewater treatment plants. It may also be used to treat wastewater flows from sludge dryers and incinerators. SHARON is a biological nitrification/denitrification process operating with minimal sludge retention time. Due to differences in growth rates of the bacterial species at the process design temperature (30–40°C), a selection can be made wherein the nitrite oxidizing bacteria are washed out of the system while ammonia oxidizing bacteria are retained along with denitrifying bacteria (Figure 2.1). This effectively stops the nitrification process at nitrite and prevents the formation of nitrate. The use of this metabolic mode of operation allows for a 25% reduction in aeration energy required for nitrification and a 40% reduction in the amount of BOD required for denitrification. The separate treatment of high strength ammonia liquors significantly reduces the load on the main treatment plant, thus increasing plant capacity without the need for additional basin volume (Grontmij N.V., 2008) The process has moved beyond the development stage, since several full-scale SHARON systems have been constructed at large wastewater treatment plants in several countries.

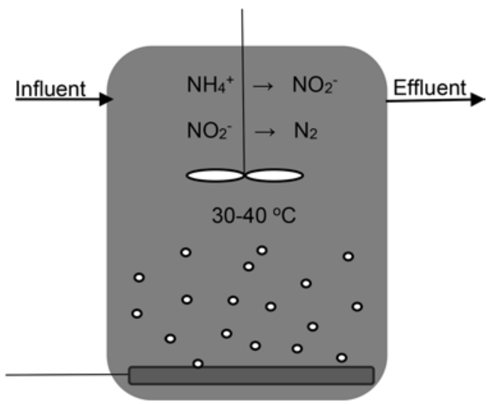

Figure 2.1 Schematic representation of SHARON.

In the ANAMMOX® reactor ammonium is converted to nitrogen gas. The reaction is carried out by two different bacteria, which coexist in the reactor. Nitrifying bacteria oxidize about half of the ammonium to nitrite. Anammox bacteria convert the ammonium and nitrite into nitrogen gas (Figure 2.2). The ANAMMOX® reactor is aerated and equipped with a biomass retention system. The reactor contains granular biomass. The wastewater is continuously fed to the reactor. The aeration provides for rapid mixing of the influent with the reactor content, intense contact with the biomass and oxygen supply to drive the conversion. The treated wastewater leaves the reactor by passing the biomass retention system at the top of the reactor. The granular biomass is separated from the cleaned wastewater, assuring high biomass content in the reactor. Together with the dense conversion properties typical for granular biomass, the high biomass content provides for high conversion rates and therefore small reactor volume. Advantages of ANAMMOX® compared to conventional nitrification/denitrification include high nitrogen removal, no methanol dosing requirement for denitrification, up to 60% reduction of power consumption, minimal production of excess sludge and up to 50% less space required (Minworth STW, 2012). In addition, up to 90% reduction of CO_2 emission is achieved which brings the plant's carbon footprint down to a minimum. In 2012, 14 full-scale ANAMMOX® reactors were under operation.

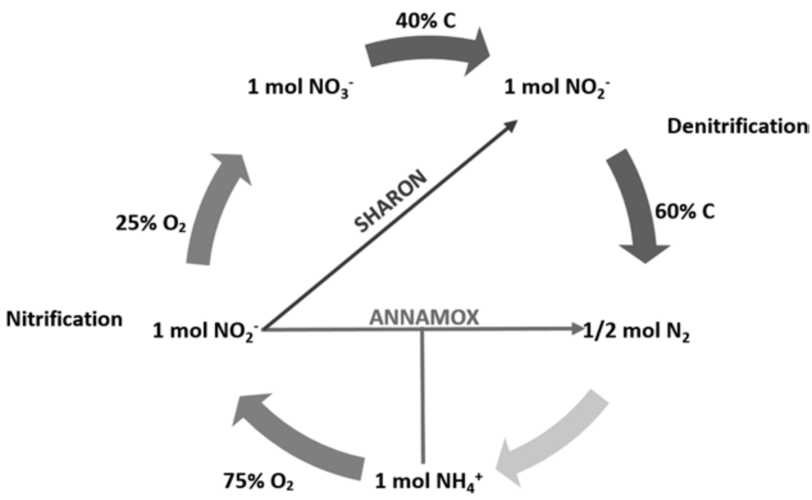

Figure 2.2 Schematic representation of SHARON and ANNAMOX.

The CANON system (Completely Autotrophic Nitrogen Removal Over Nitrite) can potentially remove ammonium from wastewater in a single, oxygen-limited treatment step. The usefulness of CANON as an industrial process is determined by the ability of the system to recover from major disturbances in the feed composition. CANON is a combination of partial nitrification and ANAMMOX in a single aerated reactor and it relies on the stable interaction between only two bacterial populations: Nitrosomonas-like aerobic and Planctomycete-like anaerobic ammonium oxidizing bacteria (Third *et al.* 2001). In the CANON system both types of bacteria can co-exist in one reactor due to oxygen and oxygen-free zones within the biofilm depth. Ammonia is partially oxidized under oxygen-limited conditions to nitrite and next nitrite together with the remaining ammonia is converted to dinitrogen gas by the Anammox bacteria. A few pilot- and full-scale applications of the CANON process are reported in the literature (Biswas R. & Nandy T., 2015).

BABE- bioaugmentation with endogenous nitrifiers: The main design criterion for a nitrifying treatment plant is the required aerobic solid retention time (SRT). By adding nitrifying bacteria to the activated sludge system it is possible to decrease the required SRT. An important disadvantage of adding bacteria in suspension is that they are susceptible to grazing by higher organisms, and not necessarily adapted to the conditions of the actual treatment process. The so-called BABE® (Biological Augmentation Batch Enhanced) technology overcomes this problem by producing nitrifying bacteria into the activated sludge flocs. To achieve this, a limited amount of activated sludge from the main process is recycled over the BABE reactor (Figure 2.3). The concept has two main goals: biological treatment of a nitrogen-rich side-stream and augmentation of nitrifying bacteria in the main stream (IWA, 2008).

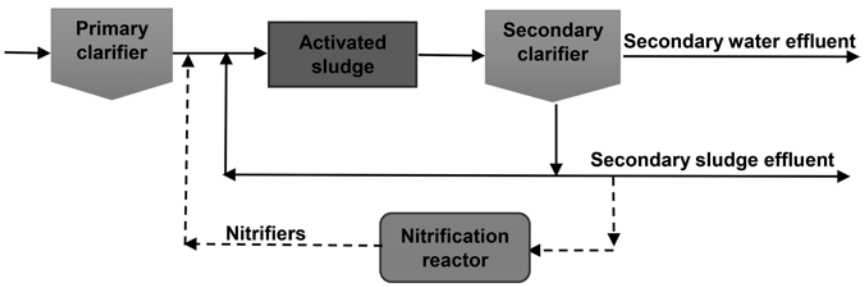

Figure 2.3 Flow chart of BABE process.

2.3 PHOSPHOROUS RECOVERY

Sewage sludge contains significant contents of nitrogen (N) and phosphorus (P), nutrients that could be recovered and reused. As fertilizer production is based mainly on non-renewable primary materials and energy resources (phosphate rock and e.g. oil and petroleum gas), the recovery of N and P from wastewater streams to produce fertilizers and compost, as well as the achievement of high added value products, will have major environmental impact through reduced CO_2 emissions, waste production and primary resource protection.

In terms of phosphorus, its demand for fertilizer production is growing steadily due to increasing world population and welfare. For Europe, P becomes a strategic resource because hardly any primary resources (phosphate rock) are available. This dependency of Europe on phosphorus imports threatens our future food security. The extensive use of P fertilizers in agriculture has increased and prices soared by 800% between 2006 and 2008. The limited P sources available and the inefficiency of the P fertilizer production process (only one fifth of the phosphorus in the rock that is mined actually makes its way into our food) is a serious problem which will eventually lead to further fertilizer price increase, increasing environmental pollution, energy and resource consumption (European Sustainable Phosphorus Platform, 2015).

Given the fact, that most of the phosphorus entering a wastewater treatment plant ends up in the sludge, three principle routes exist for closing the phosphorus cycle by recovery from the wastewater: application of sludge to land, recovery of phosphorus from sewage sludge ash and physicochemical processes that aim to concentrate and remove phosphorus from sludge (Table 2.1).

Table 2.1 Processes for P recovery from wastewater streams.

Technology	Process	Advantages/ Disadvantages	P Form
MAP	Magnesium Ammonium Phosphate (MAP, Struvite) is generated through crystallization among PO_4^{3-}, NH_4^+ and Mg^{2+}. Chemicals are added to wastewater including high phosphorous concentration such as digester supernatant, and they are stirred and mixed with aeration.	Easy operation, no need for MAP pretreatment, low running cost, NH_4^+ is simultaneously removed. NH_4^+ is required. Not suitable for low phosphorous concentration wastewater.	MAP
HAP	Hydroxyapatite (HAP) is generated through crystallization among PO_4^{3-}, Ca^{2+} and OH^-. Chemicals are added to wastewater including low P concentration such as secondary effluent, and they are sent to crystallization reactor.	Few by-product, low running cost. Degassing and filtration are required. Difficulty to maintain seeding grain.	HAP
Electrolysis	After immersing iron electrode under wastewater and passing DC, Fe^{2+} is eluted from positive electrode, being oxidized to Fe^{3+} by dissolved oxygen and phosphate is precipitated reacting with Fe^{3+}.	Simple equipment, possibility to small-scale facilitated. Maintenance of electrode to avoid the generation of iron hydroxide layer on its surface.	$FePO_4$
Adsorption	Secondary effluent is sent to packed tower filled with Zr, activated alumina adsorbent and phosphate is removed, while the adsorbent is reused.	Low sludge generation, variety of adsorbents. Easily affected by coexisting materials.	Phosphoric acid, calcium phosphate

2.4 THE MEMBRANE BIOREACTOR PROCESS

The MBR process was developed to provide high quality effluents on constrained sites. It can be tailored to provide reuse quality effluent or adapted specifically for nutrient removal (Parker, 2011). Membrane Bioreactors (MBR) integrate a perm-selective or semi-membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and are now widely used for municipal and industrial wastewater treatment with plant sizes up to 250,000 population equivalents. With the MBR technology, it is possible to upgrade old wastewater plants (Fitzgerald, 2008).

Membrane Bioreactors combine conventional biological treatment (e.g. activated sludge) processes with membrane filtration to provide an advanced level of organic and suspended solids removal. When designed accordingly, these systems can also provide an advanced level of nutrient removal. In an MBR system, the membranes are submerged in an aerated biological reactor (Figure 2.4). The membranes have pores ranging from 0.035 μm to 0.4 μm (depending on the manufacturer), which is considered between micro and ultrafiltration. This level of filtration allows for high quality effluent to be drawn through the membranes and excludes the sedimentation and filtration processes typically used for wastewater treatment. Because the need for sedimentation is eliminated, the biological process operates at a much higher mixed liquor concentration, in the 1.0–1.2% solids range, which is 4 times that of a conventional plant. This dramatically reduces the process tankage required and allows many existing plants to be upgraded without adding new tanks (Figure 2.5). The decreasing cost of membranes makes MBRs favorable and it is recognized as the future technology for wastewater treatment.

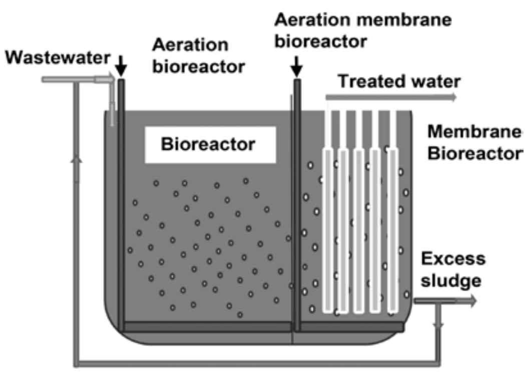

Figure 2.4 Typical submerged MBR.

With MBRs, biological-solids residence times (SRTs) are increased, enabling more complete biological treatment and retention of pathogens (including viruses); treatment with MBR produces a highly clarified effluent that can be more easily disinfected. Thus, treatment with MBR produces non-potable water. For the reclamation of potable water, MBR must be followed by RO and UV treatment (Tao *et al.* 2005, 2006).

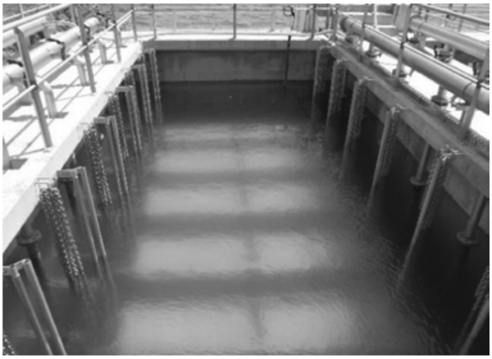

Figure 2.5 Upgrade with MBR of the wastewater treatment plant of Aigio city, Greece for 30,000PE.

2.5 ADVANCED OXIDATION PROCESSES (AOPs)

Advanced oxidation processes, involve a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and wastewater by oxidation through reactions with hydroxyl radicals ($^{\bullet}OH$). These reactive species are the strongest oxidants that can be applied in water and can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. Consequently, $^{\bullet}OH$ react unselectively once formed and contaminants are quickly and efficiently fragmented and converted into small inorganic molecules (Figure 2.6). The main mechanism of AOPs function is the generation of highly reactive free radicals.

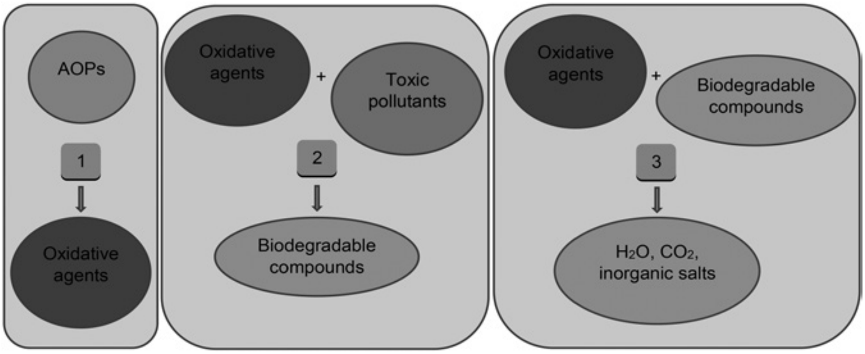

Figure 2.6 The 3-step mechanism of AOPs processes.

Hydroxyl radicals (•OH) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and non-selectively with nearly all electron-rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions compared to conventional oxidants such as H_2O_2 or KMnO4 (Gogate & Pandit, 2004).

Hydroxyl radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide). Advanced oxidation processes include combinations of ozone, ultraviolet (UV) light, and hydrogen peroxide to create the highly reactive hydroxyl radical (•OH). In addition, activated carbon is still widely used for water reclamation.

The great interest of the academic community for the use of AOPs in wastewater treatment is reflected by the significant number of publications that have been produced during the last decade. So far, TiO_2/UV light process, H_2O_2/UV light process and Fenton's reactions have been extensively used for the removal of COD, TOC, dyes, phenolic compounds, endocrine disrupting chemicals and other recalcitrant organic chemicals from industrial and municipal wastewater. The major factors affecting these processes are the initial concentration of the target compounds, the amount of oxidation agents and catalysts, the light intensity, the irradiation time and the nature of the wastewater's solution (pH, presence of solids and other ions). The role of the aforementioned parameters on AOPs performance has been sufficiently described for different types of wastewater (Stasinakis, 2008). However, although there has been much progress in understanding AOPs, most work has been limited to laboratory or pilot-plant scale; there are few reports on industrial applications of AOP for wastewater treatment and hardly any disclose costs (Vogelpohl, 2007).

However, several topics such as the relatively high operational cost of these processes due to the use of costly chemicals and the increased energy consumption, as well as the formation of unknown intermediates which in some cases could be more toxic than the parent compounds remain unsolved. Moreover, all these methods are susceptible to scavenging of hydroxyl radicals by non-target substances, while they are not suitable for certain categories of toxic compounds which resist attack by hydroxyl radicals.

The application of separation steps such as coagulation, sedimentation, filtration before the application of AOPs could remove solids that interfere with these processes. Moreover, the use of AOPs, as a pretreatment step which is followed by biological treatment processes, could achieve lower cost and sufficient organic compounds removal (Stasinakis, 2008).

2.6 SLUDGE TREATMENT AND DISPOSAL

Sludge and low quality water (treated wastewater) are the main products of the wastewater treatment plants. Although water reclamation and reuse has been significantly increased during the last few years, the management and the final disposal of sludge still remains a problem. During the 1980s there was a strong conviction that digested and dewatering sludge could be used as a high quality fertilizer. However, the evolution of analytical equipment revealed that sludge absorbs all non-biodegradable substances as well as xenobiotics and heavy metals. Thus, the use of sludge requires extensive monitoring to avoid undesirable situations. In addition, the continuous development of new chemical substances which are not known by the microorganisms makes unavoidable the existence of undesirable substances in treated sludge at least at low concentrations. Thus, the final disposal of this product still remains problematic.

The problem is worse in developing countries. For example, large amount of sludge has caused big troubles and raised significant concerns in China (Yang *et al.* 2015). The total sludge production in China had an average annual growth of 13% from 2007 to 2013, and 6.25 million tons dry solids was produced in 2013. Per Capita sludge production in China is lower than that in developed countries; however, its management is still poor. As for sludge treatment and disposal, many technical routes have been applied. Thickening, conditioning, and dewatering are the three most used treatment methods, while application ratios of stabilization and drying are low. More than 80% of sludge is disposed by improper dumping in China. Regarding proper disposal, sanitary landfill is the most common, followed by land application, incineration and use for the production of building materials.

Figure 2.7 shows the main actions taken for sludge treatment and disposal in developed countries. Digestion, dewatering, drying and disposal are the four steps for the integrated sludge management.

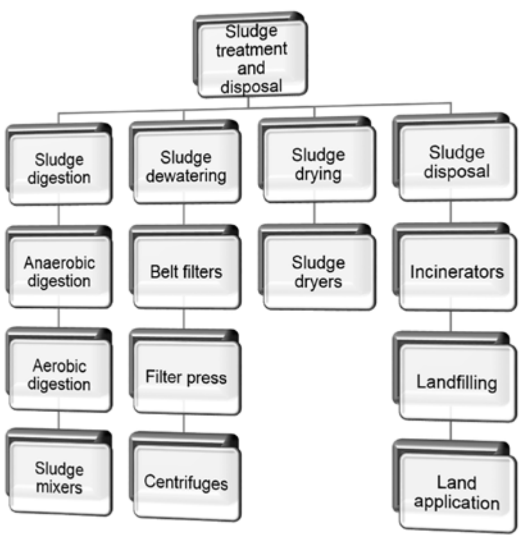

Figure 2.7 Sludge treatment and disposal options.

For wastewater treatment, plants with a capacity higher than 100,000 PE, primary sedimentation and consequently anaerobic digestion of sludge is necessary. In any case, water removal from sludge is essential since only 20–30% of solids concentrate after dewatering. Thus, drying is necessary especially for bigger capacity plants (Figure 2.8).

Figure 2.8 Dried sludge from the drying unit of Thessaloniki (Greece) wastewater treatment plant.

Solar drying of sewage sludge has become a generally accepted ecological and economical technology. It is relatively easy to implement and to handle, and operating costs for electricity and heat are low. In addition, the amount of pathogens in sludge solids can be reduced by solar UV radiation and the high reduction of water content. Therefore, with this drying technology sludge solids which are suitable for agricultural reuse can be produced. Worldwide, a huge number of solar sludge drying plants are already operating. Experience on constructing and operating these plants is sufficient, however design rules, especially for different climatic regions are not available. Solar drying is a low cost approach for sludge drying but for lower capacity plants due to increased land requirements.

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Chapter 3

Nonel biological processes for nutrient removal and energy recovery from wastewater

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3.1 INTRODUCTION

Wastewater is the used water arising from human activities at household, commercial and industrial level. By its etymology, "wastewater" implies that it is about water which has been wasted having lost its original value. In fact, its value in terms of energy and material content remains high (Verstraete & Vlaeminck, 2011; McCarty *et al.* 2011). In order to avoid the negative impact of the term "wastewater" on the public perception, another term has been proposed: "used water" (Verstraete & Vlaeminck, 2011). The ultimate goal of making the public thinks differently about wastewater and, particularly, municipal wastewater, is to promote water recycling. After all, even fresh water is recycled water, since it follows the hydrologic cycle from the final treated wastewater receptors (rivers, lakes, oceans) to condensate forms in the sky (clouds) and finally back to the ground through the precipitated forms (rain, snow) which enrich the aquifer.

In general, the recovery of energy, nutrients, organic fertilisers and water has been the new perspective in wastewater treatment in an attempt to reduce the cost and save the resources. The conventional municipal wastewater treatment plant (WWTP) succeeds in reducing the common pollutants of municipal wastewater (organic carbon, nitrogen, phosphorous) to environmentally acceptable levels. However, the operation of conventional WWTP is costly and energy intensive and has high environmental footprint. Usually, all three aspects are interconnected, since, due to the high energy demands which are met with using fossil fuels, the operating costs get high. Specifically, Verstraete and Vlaeminc (2011) estimated that the cost varies from 17–30 €/PE/y to 30–40 €/PE/y for big and small WWTPs respectively, and the 30–38% of this cost concerns the operational costs. The energy demand is estimated to be 33 kWh/PE/y, the 20% of which is recovered through anaerobic digestion of sludge. Even the most energy efficient WWTPs require 20 kWh/PE/y, 50% of which is recovered through anaerobic digestion of sludge. The high environmental footprint is due to the electricity consumption not only for the operation, but also for the construction of WWTP, the sludge transfer, the production of chemicals needed to be added in WWTPs. It is also owed to the production of greenhouse gas emissions (CH_4, nitrous oxides).

The present chapter focuses on novel technologies based on bioprocesses mainly aiming to reduce the energy consumption in WWTPs: efficient biological nutrient removal and anaerobic processes extended to raw and pre-concentrated wastewater. Bioelectrochemical systems, with microbial fuel cells being the prominent system of this technology, have attracted much interest and intensive research is focused on carbon and nutrient removal aiming to increase the power output and decrease the cost. However this topic is not covered here.

3.2 BIOLOGICAL NUTRIENT REMOVAL PROCESSES

Biological nutrient removal (BNR) has been proposed as the environmental friendly and economic efficient alternative to physico-chemical processing of wastewater. The conventional sewage sludge process focuses on carbon removal (secondary treatment), while nutrient removal is achieved at an upper level (tertiary treatment). It is found more effective to combine carbon with nutrient removal which is based on the alternation of aerobic, anoxic and anaerobic conditions. Malamis *et al.* (2015) overviewed integrated schemes of carbon and nutrient removal in Europe and Northern America and reported the cost of new installations against the cost of retrofitting existing WWTPs for incorporating BNR processes. It was found that the cost of new installations is influenced primarily from the influent loads and the effluent requirements, while the cost of retrofitting is more site specific and for this reason varies a lot (capital cost: from 16 \$ per m^3 d^{-1} to 5234 \$ per m^3 d^{-1}) even for installations of similar capacity. Generally, the total cost of a new installation is greater than the retrofitting of existing installation.

In typical BNR systems, conventional nitrification/denitrification process takes place for the conversion of ammonium nitrogen (NH_4^+–N) to gas nitrogen (N_2), and biological phosphorous removal takes place with the accumulation of phosphorous in the form of polyphosphate molecules in the bacterial cells. In conventional nitrification/denitrification (Figure 3.1), a series of transformations of nitrogenous compounds classified in two stages consists of (a) the ammonium (NH_4^+) oxidation to firstly nitrite (NO_2^-) by the Ammonium Oxidising Bacteria (AOB) and then to nitrate (NO_3^-) by the nitrate oxidising bacteria (NOB) and (b) the reduction of nitrate to nitric oxide (NO), nitrous oxide (N_2O), and finally to nitrogen gas (N_2) by the denitrifying bacteria. Both AOB and NOB are autotrophic and aerobic while the denitrifying bacteria are heterotrophic and anoxic (Tchobanoglous *et al.* 2003).

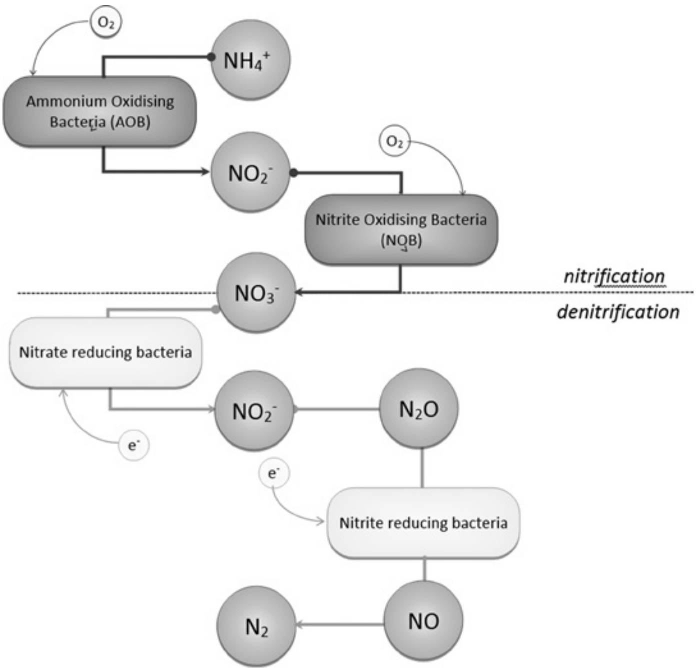

Figure 3.1 Conventional nitrification/denitrifiacation process.

On the other hand, biological phosphorus removal is based on the ability of phosphorus accumulating organisms (PAOs) to form polyphosphate chains concentrating phosphorous up to 10% of their dry weight. PAOs when exposed to alternating aerobic and anaerobic conditions are getting stressed. As a result of the stressful conditions, they choose to form volatile fatty acid polymers (polyhydroxyalkanoates; PHAs) from volatile fatty acids (VFAs) in anaerobic conditions. The energy required for this buildup derives from the breakdown of the polyphosphate chains already present inside their cells. The result of polyphosphate breakdown is the release of phosphates outside their cell. When aerobic conditions are settled, PAOs break down the PHAs to form new cells and the products of the aerobic catabolism (CO_2, H_2O). The energy released is being stored in the phosphate bonds of new polyphosphate chains which are formed in this phase by uptaking the phosphates from the bacterial environment (Figure 3.2). In this way, the anaerobic phase of the next cycle may begin. When biomass is removed in the aerobic phase, phosphate is also removed in the form of polyphosphates (Tchobanoglous *et al.* 2003).

In BNR systems all three phases (aerobic, anoxic and anaerobic) are combined in space (i.e. in separate compartments of the same tank or different tanks) or in time (i.e. through intermittent aeration of the same tank as happens in sequential batch reactors, SBRs). The anaerobic phase is usually placed upstream before the aerobic/

anoxic phases for the PAOs to take up the volatile fatty acids of the wastewater. The succession of aerobic and anoxic phases can be set up with the anoxic phase placed first for the denitrifiers to use the organic matter of the incoming wastewater. In this case internal recirculation of the mixed liquor from the aerobic to the anoxic phase is necessary to provide the denitrifiers with the nitrates (Figure 3.3 presents an example of the combination described above).

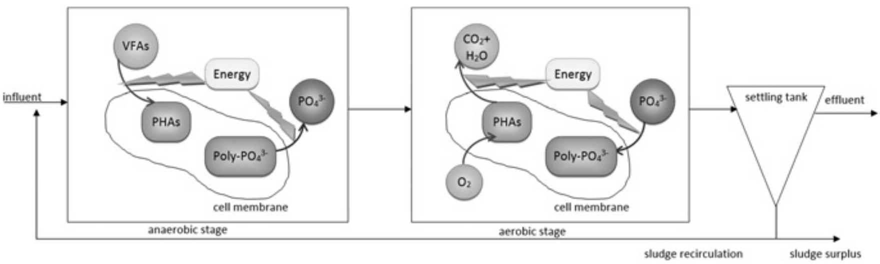

Figure 3.2 Biological phosphorous removal.

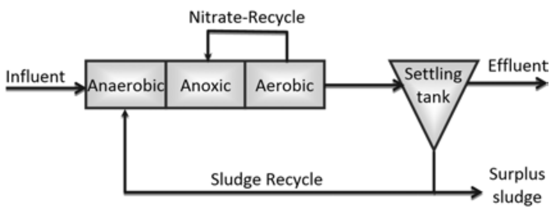

Figure 3.3 BNR process combining phosphorus and nitrogen removal.

Integrating the BNR process with the carbon removal process increases the operating cost due to additional aeration requirements, the internal recirculation streams and the addition of an organic source in the anoxic and/or anaerobic phase for the dentitrifiers and PAOs respectively in case the organic content of the wastewater does not suffice. The aeration is responsible for the largest consumption of the electricity (50–70%) in a WWTP (Verstraete & Vlaeminc, 2013; McCarty *et al.* 2013; Malamis *et al.* 2015). The energy consumption for aeration can be reduced through efficient oxygen transfer technologies (micro-bubble distributors, Terasaka *et al.* 2011; bubbleless aeration in membrane aerated biofilm reactors-MABR, Timberlake *et al.* 1988; Shanahan & Semmens, 2006). Specifically, in the MABR technology the membranes serve as a means to provide oxygen through diffusion but also as a supporting material for the formation of biofilm. Although biofilm formation was seen initially as a disadvantage leading to membrane fouling, it actually resulted in the increase of the residence time of oxygen in the reactor. This technology is also suitable for cases where the bubbling air causes undesired stripping of VOCs (volatile organic compounds) (Kniebusch *et al.* 1990) and foaming (Pankhania *et al.* 1999) as well as for cases of high organic loading wastewaters (Yamagiwa *et al.* 1994) and BNR (Timberlake *et al.* 1988).

A significant breakthrough in air saving occurred with the discovery of skipping aerobic nitration through partial nitrification/denitrification and anammox processes. In partial nitrification/denitrification, ammonium is oxidised to nitrite which is reduced to nitrogen gas (Figure 3.4). Anammox (or else anaerobic ammonia oxidation) process is mediated by autotrophic anaerobic bacteria which couple the NH_3–N oxidation with the NO_2–N reduction so that N_2 is formed. The NO_2–N may derive from partial denitrification ($NO_3^- \rightarrow NO_2^-$) where the organic carbon needed is less than full denitrification or from partial nitrification (nitritation) where the oxidation of NO_2^- to NO_3^- is inhibited. In the latter case, no organic carbon is needed (Figure 3.5). A side product of anammox process is NO_3^- which is produced at 10% of the initial NH_3–N.

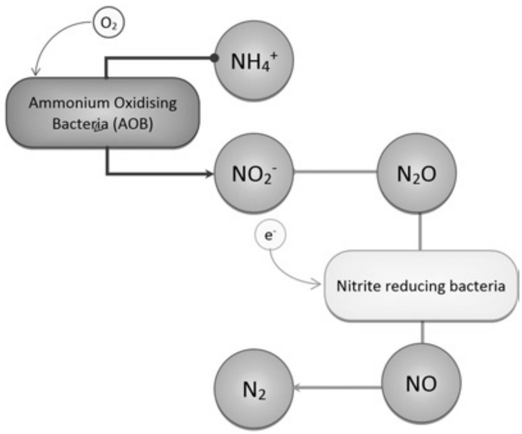

Figure 3.4 Partial nitrification/denitrifiacation process.

However, the amount of oxygen saved is not directly related to the oxygen need for the nitration step. Generally, the oxygen demand for complete ammonium nitrogen oxidation (4.57 kg O_2/g NH_3–N oxidised) is higher than that required for organic carbon oxidation (0.7–1.5 kg O_2/kg BOD_5 removed) (Technical Bulletin 135, 2012). However, oxygen can be partially recovered during denitrification (2.86 kg/kg NO_3–N) if the influent wastewater is used as a carbon source. Since the electron flow from NH_3–N to N_2–N is the same regardless the route chosen, the net oxygen demand for nitrogen removal is much lower: 1.71 kg O_2/g NH_3–N removed (Daigger, 2014). In this sense, novel BNR technologies based on skipping the aerobic nitration should be chosen on the availability of the carbon to nitrogen ratio; since the organic loading to these processes is reduced, the surplus organic load could be captured upstream to be used for energy production through anaerobic digestion, while the remaining could be utilised by the bacteria involved in these processes without the need to add extra organic source. Suppressing the oxidation of nitrite to nitrate and its subsequent reduction steps reduces the requirement of oxygen by 25% and carbonaceous COD (for the denitrification step) by 40%. It also results in less sludge and CO_2 production by 30% and 20% respectively (Gustavsson, 2010).

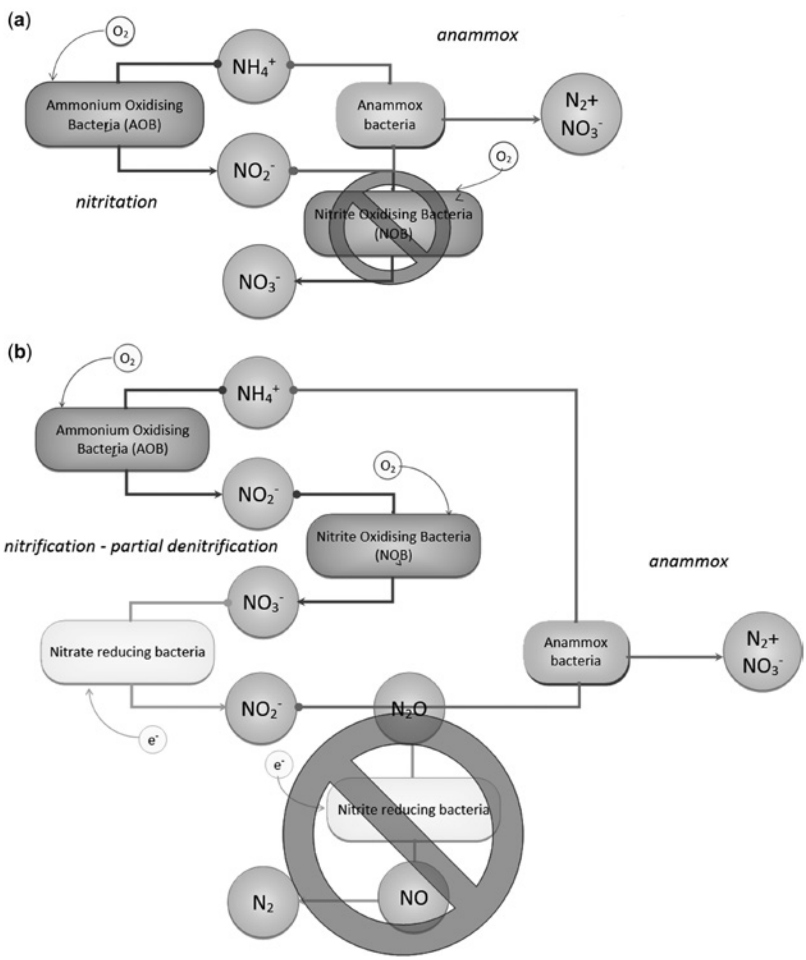

Figure 3.5 Anammox process coupled with (a) nitritation and (b) partial denitrification.

The key issue to partial nitrification/denitrification is the effective accumulation of nitrite, by promoting the growth of the ammonium oxidizing bacteria (AOB) at the expense of the nitrite oxidizing bacteria (NOB) (Malamis *et al.* 2014). Selection of appropriate conditions contribute into this goal; low dissolved oxygen concentrations (0.4–1.0 mg/L) favour growth of AOB (Blackburne *et al.* 2008a) and so does a high temperature range (30–40°C) (Hellinga *et al.* 1998). Strategies for depleting NOB which are based on the dissolved oxygen concentration include the alternation of anoxic and aerobic conditions (Gilbert *et al.* 2014) and the aeration time control through monitoring of dissolved oxygen, oxidation reduction potential and pH (Blackburne *et al.* 2008b; Gu *et al.* 2012). Moreover, high free ammonia concentration (>1 mg NH_3/L) or high free nitrous acid concentration (>0.02 mg HNO_2–N/L) inhibit NOB (Vadivelu *et al.* 2007; Gu *et al.* 2012). The combination of the aforementioned conditions results in further enhancement of the nitritation step (Sun *et al.* 2013; Katsou *et al.* 2015).

Partial nitrification/denitrification has been successfully applied to wastewaters with high ammonium to carbon ratios such as reject water (Frison *et al.* 2013), leachates from landfills (Sun *et al.* 2013) etc. The carbon needed in these cases can be derived from short chain carbon compounds produced from the fermented sewage sludge. In this way, the cost for carbon supply is reduced while the nitritation/denitritation as well as denitrifying phosphorus removal via nitrite is promoted. According to US EPA (2013), the treatment of reject water through nitritation/denitritation is an innovative process with very few full scale applications worldwide.

The anammox technology has emerged with the discovery of the anammox bacteria which possess special organelles performing the unique oxidation of ammonium anaerobically with nitric oxide and hydrazine as basic intermediate compounds (Kartal *et al.* 2013). Several drawbacks exist for the stable anammox process to be established in the wastewater treatment technology; they can be categorised to those related to the physiology of the anammox bacteria (slow growth rate) and the operating conditions (coexistence of the aerobic AOB and the anaerobic anammox bacteria or the autotrophic anammox and the highly competing heterotrophic denitrifiers).

Anammox bacteria grow very slowly; doubling times vary between 15 and 30 days (Lotti *et al.* 2015) and the growth yield is low (0.11 g VSS/g NH_4^+–N) (Strous *et al.* 1998). This was the main reason why these bacteria could not be isolated and enriched. In order to increase the growth rate, the anammox is usually restricted to high temperatures of 25–40°C (Zhu *et al.* 2008) and organic carbon to ammonium nitrogen ratio lower than 0.5 g COD · g N^{-1} to avoid competition by the heterotrophic denitrifiers (Jenni *et al.* 2014). However, bioreactors operating at high solid retention times under specific operating strategies would adapt anammox bacteria to perform at higher rates. Lotti *et al.* (2015) showed that anammox bacteria were able to grow at a fourfold higher rate through proper "training" in a membrane bioreactor (MBR). Jenni *et al.* (2014) succeeded in increasing the COD to N ratio stepwise to 1.4 in a bioreactor with granulated anammox biomass. Several strategies of adaptation are reviewed in Ma *et al.* (2016), Kartal *et al.* (2013) which aim to show that anammox through proper adaptation could compete the conventional biological processes for nitrogen removal.

In biofilm and granular bioreactors, the formation of biofilm or granular sludge also provide a practical functionality; the bacteria in these formulations are organised in layers where the outer layers are occupied by the AOBs exposed to aerobic conditions and produce nitrite for the anammox bacteria occupying the inner layers where anaerobic conditions prevail. Ma *et al.* (2016) summarises the importance of biofilm or granule formation by anammox especially in the cases of low strength wastewater loading at high influent rates and low temperatures (20°C or lower in winter). Both high influent rates and low temperatures favour the excretion of extracellular polymeric substances (EPS) which are responsible for these bacterial aggregates. However, the low temperature reduces the settleability of granules due to the higher viscosity and density of water in these conditions. For this reason it is advised to begin anammox granulation during summer. Moreover, the over excretion of EPS may block the pores of granules trapping the gaseous N_2 formed within and make the granule buoyant leading it to washout. The size of granules should be kept below 2.20 mm to prevent floating (Ma *et al.* 2016). The oxygen penetration through the film is also influenced by the biofilm thickness; in fact there is an optimal level in dissolved oxygen concentration and thickness of biofilm depending on the surface loading of ammonia (Hao *et al.* 2002).

Anammox bacteria are considered to be sensitive to oxygen and coexistence with the aerobic AOBs in single stage bioreactors may be tricky. Since oxygen levels must be kept low in order to deplete NOBs, an oxygen deficient environment may not be detrimental to anammox bacteria. Moreover, wherever non homogeneity prevails (e.g. in heterogeneous systems) anammox bacteria may aggregate in the non-oxygenated spots of a bioreactor, i.e. in the inner layers of a biofilm or granule. Adaptation also plays a crucial role in this case; Liu *et al.* (2008) managed to adapt the anammox bacteria up to 8 mg/L of dissolved oxygen with little loss of their activity after a long time of exposure to these advert conditions.

An alternative pathway for nitrite accumulation is through the denitrification process. However, the denitrification is competitive to anammox due to the higher change in the Gibbs free energy in the respective reactions as well as the higher yield and growth rate of dinitrifiers compared to anammox bacteria (Rittmann & McCarty, 2001).

Denitrification:

$$\begin{aligned} NO_3^- + 0.625CH_3COO^- + H^+ &\rightarrow 0.5N_2 + 0.625CO_2 \\ &+ 0.625HCO_3^- + 1.125H_2O, \quad \Delta G\circ = -498\ kJ/mol\,NO_3^- \end{aligned}$$

Anammox:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O, \quad \Delta G\circ = -358\ kJ/mol\,NH_4^+$$

The carbon to nitrogen ratio plays also important role for the coexistence of anammox bacteria and denitrifiers since at high C/N ratios, methanogenisis may be competitive to denitrification. However, at high C/N ratios the change in the Gibbs free energy is less favourable but the dissimilatory nitrate reduction to ammonia may prevail due to excessive reducing power. A suitable range for C:N is between 0.8 and 1.6, while the ratio of NH_4^+:NO_2^- is between 1:1 and 1:5. Dissolved oxygen also influences this coexistence as well as temperature and pH (Kumar *et al.* 2010).

The technological advances of anammox process include mainly the configurations consisting of single or multi-stage bioreactors operating at high retention time, strategies for the start-up and operation of anammox systems. In single stage systems nitrite is produced in a O_2 deficient environment (CANON), while in two-stage systems nitrite is produced separately in an aerobic bioreactor and fed into an anoxic anammox bioreactor (SHARON). Many more names accompany anammox technology, but basically all modifications can be distinguished according to the number of stages included (Hu *et al.* 2013). In principle one-stage systems are featured with lower investment cost, while two-stage systems offer more handling options for optimising the two stages of anammox. The choice between one and two stage systems lies primarily on site specific factors such as space availability, available budget, if it is a new installation or retrofit of an existing one.

The bioreactors known for their high solid retention time, such as upflow anaerobic sludge bed (UASB), biofilters, gas lift reactors, membrane reactors (MBR) and sequential batch reactors (SBR) have been used successfully for anammox. UASB has been proven robust under increases in hydraulic or substrate loadings and MBR has the capacity to retain the biomass effectively in unstable conditions (Jin *et al.* 2008; Wang *et al.* 2012). The full scale plants for treating primarily ammonium rich wastewaters of various origins (reject water, tannery, food processing, semiconductor, fermentation, yeast, distillery, winery industries) reached almost 100 in 2014 (Lotti *et al.* 2014). Common values of the influent COD/NH_4^+ vary from 0.3 to 15 and the loading rates from 0.045 to 0.65 kg N $m^{-3}d^{-1}$ for SBR and 1 to 7 kg N $m^{-3}d^{-1}$ for biofilm based systems (Lackner *et al.* 2014). The energy demand for SBR-partial nitritation/anammox system has been recorded to be 0.8–2 kWh/kg N, much lower (almost 50% lower) than the conventional nitrification/denitrification process in the same installation in Ingolstadt (Germany). Intensive research is going on and continuous progress is being recorded for the capacity of these intriguing bacteria to adapt and be used in more versatile applications in future (Hu *et al.* 2013). Start-up duration varies from 19 to 465 d but the higher values in this range have been reported most frequently (Nozhenvikova *et al.* 2012; He *et al.* 2015). This is one of the main obstacles hindering the wide application of anammox. It can be overcome through efficient cultivation and long term storage of the seeding inoculum (He *et al.* 2015).

Nitrous oxide (N_2O) is a greenhouse gas which induces 300 times more global warming than CO_2. It is an intermediate of conventional denitrification and a side product during ammonia oxidation when the two stages ammonia oxidation are imbalanced (which is the case of novel BNR). N_2O emissions can be mediated by minimising aerobic N_2O production and emissions and maximising anoxic N_2O consumption (Desloover *et al.* 2012). Novel BNR technologies presented in this chapter are based on the imbalance of ammonia oxidation steps, but the N_2O produced is not equal to the amount that is emitted since the combination of many factors (diffusion, mixing, stripping through aeration, wind advection) determine the final outcome. Obviously, aeration facilitates mass transfer of N_2O to the atmosphere and optimising the aeration efficiency also affects positively the escape of N_2O. According to Kartal *et al.* (2011), N_2O is not involved in the anammox metabolism. However, imbalanced ammonia oxidation steps and low COD to N ratios seem to be responsible for N_2O and further investigation is needed to evaluate the emissions in one and two stage anammox systems and compare them to emissions from conventional processes (Hu *et al.* 2013).

On the other hand, N_2O has emerged as an energy source since it can be used as a co-oxidant in methane combustion or it can be decomposed to N_2 on a metal oxide catalyst through a novel technology called Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO). Combustion of methane with N_2O yields 30% more energy than the conventional methane combustion with oxygen (Gao *et al.* 2014):

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O(l) + 4N_2, \quad \Delta H^\circ_R = -1219 \text{ kJ/mol } CH_4$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(l) + 4N_2, \quad \Delta H^\circ_R = -890 \text{ kJ/mol } CH_4$$

However, this option is far away from full scale implementation since CANDO is based on the accumulation of N_2O which is an undesired product for now and all efforts are focused on minimising its production.

3.3 ANAEROBIC TECHNOLOGIES

The consumption of energy in WWTPs can be reduced through the recovery and re-utilisation of energy already contained in wastewater. This energy is chemical (captured in the bonds connecting the atoms of the pollutants) as well as thermal (due to the temperature of the wastewater). The chemical energy can be calculated through the COD. Specifically, 1 kg COD contains 3.86 kWh. The COD in municipal wastewater exists mostly in dissolved form and is mineralised fast through the well-established activated sludge process. However, during this conversion, the COD and its potential energy is "lost" by almost 50% to CO_2 and H_2O, while the remaining COD is converted to microorganisms (activated sludge). In this way, a lot of energy is lost in conventional WWTP (via the electricity supply) with the ultimate outcome of "losing" half of the captured energy in the wastewater which could be recovered if anaerobic digestion was implemented. The energy consumption can be classified to the direct consumption and the non-recovered energy forms.

The application of anaerobic digestion in WWTP has been traditionally restricted to the treatment of sewage sludge. Sewage sludge is usually a mixture of primary sludge (containing the solids of the sewage) and secondary or activated sludge (containing the biological solids from the microorganisms' growth during the secondary treatment). Although the process is stable and well established, the major problem of disrupting the solids from the activated sludge process – still remains. Various pretreatment methods (mechanical, ultrasonic, chemical, thermal and biological) have been developed to enhance anaerobic biodegradability by increasing the rate of the hydrolysis step of the particulate matter (Stamatelatou *et al.* 2012). Besides the increase of biogas yield, pretreatment methods result in the improvement of dewaterability of the digested sludge (Xu *et al.* 2011).

There is a plausible concern if the cost induced by applying a pretreatment method is compensated by the increase in the biogas production. The answer is not straightforward since factors such as the final use of biogas (for heat and electricity production, as vehicle fuel or disposed in the natural gas grid) and the digested sludge (as a soil fertiliser, solid fuel or pyrolysis oil fuel) influence the economics of the integrated anaerobic technology as well as its environmental impact (Mills *et al.* 2014).

The development of a biogas unit within a sewage treatment plant to perform codigestion with more feedstocks than sewage sludge (glycerol, agricultural wastes, energy crops, landfill leachates, food wastes) would increase the methane potential. The economic evaluation of such biogas units based on the investment decision tool presented by Karellas *et al.* (2010) shows that the factors influencing the economic viability of such a project are (a) the physicochemical characteristics of the various feedstocks, (b) their availability, (c) their gate fees if they are products of industrial activities or their cost if they are cultivated biomass, (d) the market prices for the end products, (e) the investment and operating costs and (e) the incentives such as loans, existing subsidies and grants.

Another approach of recovering the chemical energy of wastewater is to apply anaerobic digestion directly to the incoming sewage. The main obstacles of this option are the low organic load of sewage (compared to other feedstocks) and the high volumetric flowrates which result in the washout of the anaerobic microorganisms. It has been restricted to countries with warm climate such as Brazil, Colombia and India using UASB reactors at ambient temperatures. The performance is quite satisfactory (70–80%) (Vieira *et al.* 1994; Campos *et al.* 2009), although stability problems may arise, especially when the sewage is stronger and the temperature fluctuates. This is the case in arid areas such as Jordan where water consumption is limited and influent COD may be above 1000 mg/L, the 70% of which is particulate. Sludge retention in the digesters through membrane technology (Lin *et al.* 2013) or periodically seeding the UASB reactors with methanogenic sludge from sewage sludge digesters (Mahmoud *et al.* 2004) seem to be effective solutions. Anaerobic Membrane Bioreactors (AnMBR), albeit the main disadvantage of membrane fouling, have gained ground in the field of low strength wastewater at low temperatures. The long solid retention times achieved in

AnMBR permit almost the complete retention of the slow growing microorganisms and enable the downsizing of the bioreactors from 1/3 to 1/5 compared to the conventional anaerobic digesters (Kanai *et al.* 2010). The membrane fouling can be improved though proper control and various membrane configurations (Cho *et al.* 2013; Aslan & Saatci, 2014; Teo *et al.* 2014; Wu *et al.* 2016). In any case, the anaerobic digestion of sewage should be combined with aerobic steps to result in the desired levels in terms of COD at much less energy (even by 90%) than the conventional activated sludge process (Khan *et al.* 2011).

In order to enhance the biogas production from sewage, the organic matter could be concentrated; at high F/M ratios (3–6 kg BOD kg^{-1} MLSS d^{-1}) the organics are adsorbed on microorganisms of the wastewater to form aggregates which can be removed easily from the bulk wastewater (Verstraete *et al.* 2009). This stream is rich in organics and can be directed to anaerobic digestion process. Other technologies for pre-concentration of the organics are membrane filtration, dynamic filter filtration, dissolved air flotation and – coagulation/flocculation by metal salt or polyelectrolyte addition in a chemically enhanced primary treatment (CEPT). The economics of the combination of pre-concentration and anaerobic digestion vary between €0.66–0.95/m^3. Moreover, if exploitation of any kind of resource coming from wastewater is achieved (water, heat, nitrogen and phosphorous recovery as well as energy production from biogas and digested sludge based biochar), a profit of almost €1/m^3 can be made according to estimates by Verstraete and Vlaeminck (2011). This means that the zero wastewater approach can be feasible.

3.4 CONCLUSIONS

There is a growing tendency to regard wastewater more an energy and material resource than a waste. In order to recover and/or save energy novel technologies are being developed. The scientific advances on biological nutrient removal processes and anaerobic digestion are huge, and what initially seemed meaningless, nowadays it proves to be feasible. Anammox based technologies has gained huge interest due to the potential of saving aeration cost, although initially there was much skepticism about the capacity of slow growing bacteria to perform the intriguing task of nitrogen removal in full scale. Nowadays numerous full scale installations are based on anammox. Membrane technology has contributed into wastewater economics in several ways (improving aeration efficiency, increasing process performance through retention of biomass, producing effluent of high quality). Anaerobic digestion is studied to become the core technology for wastewater treatment. However, there are still technological challenges to be met (regarding process stability, membrane fouling etc) and the cost for retrofitting existing plants based on conventional processes could be high. In order to meet those challenges, site specific solutions are tailored and it seems that future WWTPs will be much different in concept and design compared to what is common nowadays.

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Chapter 4

Managing reuse of treated wastewater and bio solids for improved water use, energy generation and environmental control

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4.1 INTRODUCTION

By the year 2025, as much as 60% of the worldwide population may suffer from water shortage (Pérez-González *et al.* 2012). That is due to the fact that about 70% of the worlds freshwater are used for agriculture irrigation, mainly using surface methods. In some countries, irrigation accounts for over 90% of the developed water resources (Pedrero *et al.* 2010; Vivaldi *et al.* 2013; Grattan *et al.* 2015). Water shortage is also due to the population growth and intensive pumping of high quality waters from the aquifers. In this context, the reuse of treated municipal wastewater for agriculture irrigation represents one of the most promising ways to minimize the water scarcity issues in dry regions. The main risks that are associated with reclaimed water use for irrigation stem from food contamination and human infection due to pathogens presence (bacteria, viruses, protozoa, and helminthes), soil salinization and accumulation of heavy metals and various unknown constituents and contaminants. Currently also hormones, endocrine disruptors and drugs create extra problems of water quality. The various contaminants might adversely affect agricultural production and groundwater quality by migrating and accumulating in the soil and aquifers (Kalavrouziotis *et al.* 2015; Elmeddahia *et al.* 2015).

A related issue of wastewater is the municipal sludge fraction, its' disposal and/or reuse. Although extensive investigations have been carried out referring to several aspects of wastewater reuse in agriculture, many problems related to yield and its' quality and as well the effects on plant nutrition are required as the effects of the sludge (Morgan *et al.* 2008; Hadipoura *et al.* 2015). Indeed, the long-term use of the sludge could create environmental problems and in many cases nutritional imbalances for crops.

Municipal wastewater includes soluble minerals and dissolved organic matter, which depend quantitatively and qualitatively on the background source of water and on the types and levels of treatment (Henze, 2002; Sonune & Ghate, 2004; Daims *et al.* 2006). Frequently, the effluent applied is somewhat brackish due to the content of Na, Ca, Mg, SO_4, HCO_3 and Cl as major ions. The applied effluent contains plant nutritional constituents such as nitrogen (N), phosphorous (P) and potassium (K) (Chang & Hao, 1996; Chien *et al.* 2009) as well as micronutrients (Grattan *et al.* 2015). The treated domestic wastewater application can positively affect plant growth by providing additional nutrients (Herpin *et al.* 2007), however, excess amounts of salts can adversely affect plant development as a result of their accumulation in the root zone (Clara *et al.* 2005).

The objectives of this research are first of all to study the effects of different irrigation water qualities and learn the influence of sludge composition on soil chemical properties. It will refer to the fruit quality, and secondly to understand the effects of the multivariate relationships between water characteristics and fruit composition.

The ultimate disposal of municipal wastewater sludge (biosolids) continues to be one of the most difficult and expensive problems in the field of wastewater engineering (Tchobanoglous & Burton, 1991; Axelrad *et al.* 2010). The sludge contains different materials that commonly require an individual treatment for every type of sludge components. Application of sewage sludge to agricultural land seems to be the most practical and ultimate solution as an economical beneficial due to the fact that it a common more-use method. The major benefits of sludge application are: (i) increased supply of major plant nutrients; (ii) provision of some of the essential micronutrients (Zn, Cu, Mo, Boron, and Mn), and; (iii) improvement in the soil physical properties, i.e. better soil structure, increased soil holding water capacity, and improved soil water transmission characteristics. A gradual decrease in the organic matter content of cultivated soils in the world, as a result of factors such as excessive use of inorganic fertilizers, is a worldwide phenomenon. In warm climates, such as South Africa, Mediterranean and south USA this process is accelerated due to rapid microbial decomposition of the soil organic matter. The decrease in soil organic matter content is a problem of major concern since it may lead to a deterioration of the soil physical structure and accelerated erosion.

4.2 INFORMATION SYSTEM

A challenging issue is the information regarding the origin and type of biosolids under considerations. The information system allows classifying and subsequently deciding which method to adjust for treatment and ultimately to reuses the materials for the diverse purposes. It refers as well to the economic aspects that are related to it.

The severity of the sludge problem is well demonstrated in Figure 4.1 (Giménez *et al.* 2012). The diversity of the sludge is relatively high which requires applying a series of different treatment methods For example, an important issue is the composition of the construction residual: metals are mixed with the concentrate, hence the question is whether to separate the two components or into a larger number of basic elements.

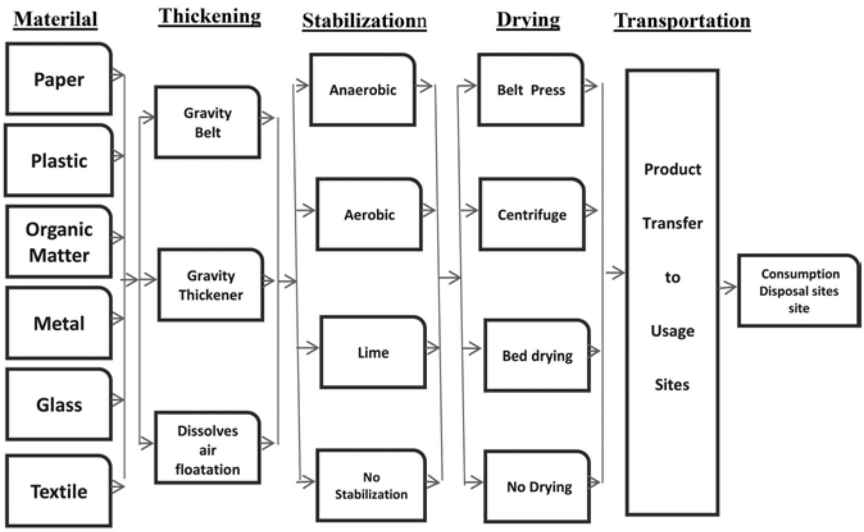

Figure 4.1 Some components of solids biowastes recycling and their reuse.

In order to treat well the sludge there is a need to first separate the main components (Sonune & Ghate, 2004; Sutherland, 2007). That approach will guarantee accepting a relatively high quality raw materials spectrum for the anaerobic stage. It will allow accepting biogas along with sludge which is advantages in regards to agricultural fertilizers. Along with it there are the environment aspects of improved control and letting the various liquids to flow freely (Chien *et al.* 2009).

There are several methods to treat the municipal solid wastes. One of the main method is based on anaerobic digestion, producing biogas (mainly a mixture of methane and carbon-dioxide) which can be used as an alternative energy source (Baek & Pagilla, 2006; Schievano *et al.* 2008; Weiland, 2010; Ryckebosch *et al.* 2011). Other methods are based on incineration and pyrolysis that leave the area with some residual materials. Advanced treatment methods are based on anaerobic Membrane BioReactors (MBR) (Elsayed *et al.* 2016; Zhen *et al.* 2016). That combination yields as well a relatively clean fertilizer, rich with nitrogen (Stellacci *et al.* 2016).

4.3 REUSE OPTIONS

This paper will focus on the reuse of municipal solids wastes, primarily for energy generation. Until recently it was believed that the reuse of solid water is not economically feasible, Currently it is believed that solids wastes can be treated and reused for energy generation, fertilizers production and may be other products as well. It can be treated under aerobic or anaerobic conditions. Energy production stems also from its' shortage worldwide and the gradual diminishing of oil. Energy production is also stimulated due to the massive growth of mega cities and the slow however, full awareness to environment issues. There is strong belief that the environment is a significant part of the modern life.

4.4 BIOGAS PRODUCTION

One of the final product of the anaerobic digestion process is the biogas, which consists of a mixture of Methane (around 65% to 75%), Carbon Dioxide (around 35% to 25%) and other small fractions of Ammonia and Sulphur. The Sulphur can be scribed out of the process since it causes corrosion of the metal pipe system. Large amounts of ammonia content are an indication that the process is not working well. The main product, methane gas can be used for divers purposes where there is a need to get rid of the Carbon Dioxide. The anaerobic digestion consists of four sub-processes, each conducted by specific anaerobic bacteria. The bacteria community is typical for the mesophilic (35°C to 38°C) and another type of bacteria is typical for the thermopile conditions (55°C to 58°C). There is always the dilemma which process to prefer: to invest: to produce more gas and invest more in mixing or to produce less energy under the mesophilic conditions. It is a worldwide issue, including the dilemma of producing some other energy source.

The anaerobic process consists in principle of four stages, namely gametogenesis, than in series the acidogenesis stage, hydrolysis and finally the methanogens stage (Chan *et al.* 2009). Under the hydrolysis stage the material is disintegrated into two monomers, allowing its' connection to other contained polymers. In the last stage of Methanogens methane gas is produced from the Acetate by the specific bacteria. Content of Carbone Dioxide and primarily of other oxidant hinders the process, namely anaerobic conditions have to be kept strictly. The caloric value of biogas is around 1000 BTU/ft^3. A schematic description of the related anaerobic stage is given in Figure 4.2.

4.5 THE MBR

The Membrane BioReactor (MBR) is a compact intense vessel which contains membranes for treating wastewater (Wei *et al.* 2003; Sutherland, 2007). In the past it was used under aerobic conditions to treat domestic wastewater (Figure 4.3). However, due to the worldwide energy crisis efforts are focused currently on energy production combined with the domestic wastewater reuse for irrigation, The MBR consists of a membrane that is submerged in a treatment vessel and treaters the raw water to acceptable levels. The membrane is an ultrafiltration membrane (0.01 μ opening, allowing mainly the passage of water. The other configuration includes an external sub-vessel with the membrane that improves the access for cleaning however is probably let effective in the treatment procedure.

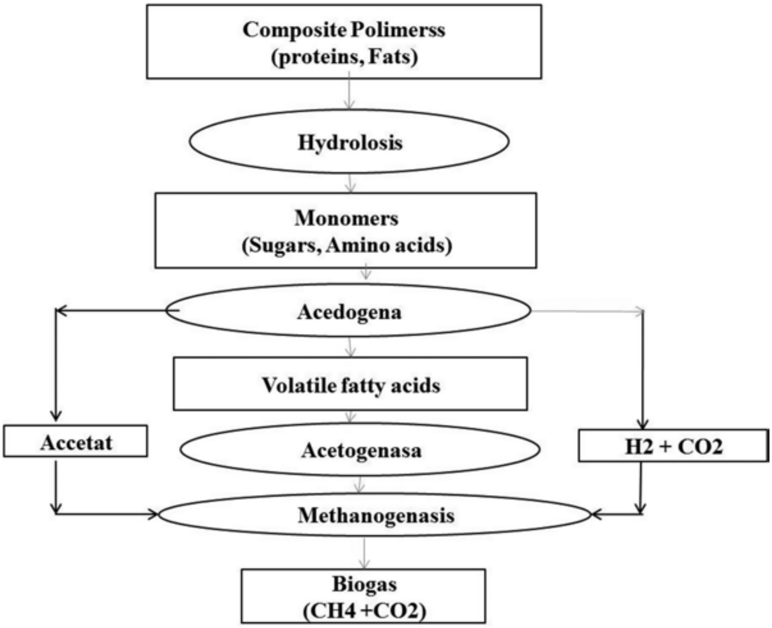

Figure 4.2 Some stages related to anaerobic digestion and biogas production.

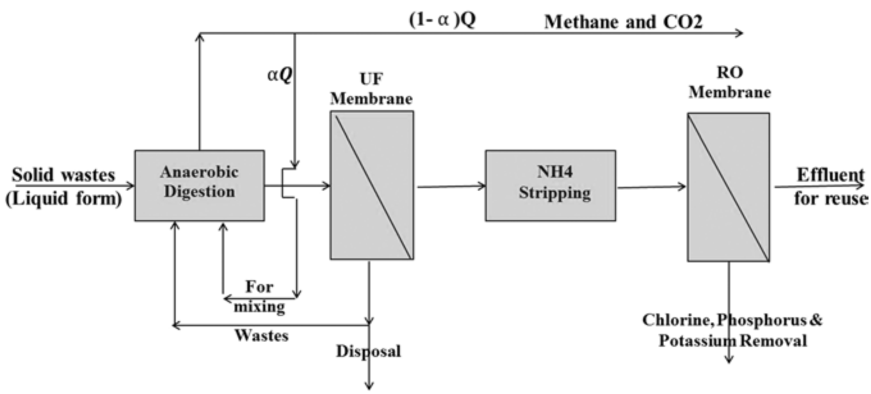

Figure 4.3 Schematic description of the principle stages taking place in an Anaerobic MBR (Q-flow of methane, m^3/h; α-fraction)

Efforts are undertaken to improve the treatment of the domestic wastewater combined with energy generation under anaerobic conditions. There is always the alternative to use part of the energy generated for mixing the biomass. These effects are currently under close observations (Giménez *et al.* 2011).

4.6 THE MAIN COMPONENTS OF BIOGAS PRODUCTION

The solid wastes contained in the wastewater consist commonly of organic matter and other minor elements. The main components that are responsible for biogas production are the organic matter, and more specifically the Total Organic Carbon (TOC) and the Chemical Oxygen Demand (COD). These constituents have a real effect of the biogas production rate. The amount of gas produced depends very much on the composition the constituents contained in the wastes and the related concentration.

4.7 SUMMARY AND CONCLUSIONS

Municipal solid wastes can easily be recycled into valuable material. Main recycled products are fertilizers for agriculture use, raw materials for construction and different forms of energy. Reaction of carbonaceous feedstock with an oxygen-containing reagent, usually oxygen, air, steam or carbon dioxide, generally at temperatures above 800°C. These processes are largely exothermic but some heat may be required to initialise and sustain the gasification process. The gas product of the gasification process is syngas, which contains carbon monoxide, hydrogen and methane. Typically, the gas generated from gasification has a low heating value since it consists of a mixture of gases. Syngas (with a calorific value of around can be used for series of purposes however, each one needs a specific investment. A cost benefit analysis is required for each purpose of utilization. Syngas can be used for the following purposes:

* Fuel use for gas turbine operation.
* It can be used as a chemical feed stock.

The liquid form of energy can be extorted as well. Mazut, which is a product of crude oil refining is product of municipal solids water recycling and is primarily used in isolated area.

The return on methane gas depends on a series of factors. These factors include the type of raw material on one side and the treatment method on the other side. In general it is in the range of \$0.2 to 0.3 per each m^3 of biogas. The content of biogas in the wastes is 0.3 to 0.4 m^3 per each kg of COD. The methane content in the mixture of biogas is around 0.75 m^3 methane per every m^3 of biogas. The above information and data allows to conduct and economy analysis everywhere, including location of low rate energy production.

4.7.1 Unit conversion

1 BTU/ft^3 = 8.9 Kcal/m^3 = 3.73 × 10^4 Joul/m^3
1 BTU/lb = 2326.1 Joul/Kg = 0.55556 Kcal/Kg

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Chapter 5

Removal of pharmaceuticals and personal care products in constructed wetland systems for wastewater treatment and management

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5.1 INTRODUCTION

Pharmaceutical and personal care products (PPCPs) are becoming ubiquitous in the environments due to their extensive applications and poor removal by the conventional wastewater treatment plants (WWTPs) (i.e. using activated sludge processes). Although the presence of these compounds in the environment corresponds to low concentration levels (ng/L to μg/L), due to their continuous release from WWTPs they still can affect water quality and ecosystem balance, and even impact drinking water resources (Verlicchi *et al.* 2012; Verlicchi & Zambello, 2014). Hence, in order to eliminate the potential risk of the PPCPs, there is a critical need to select a treatment technology that is highly efficient and has a reasonable cost of operation, in order to remove their residues from wastewaters (Klavarioti *et al.* 2009).

Constructed wetlands (CWs) due to their unique advantages such as relatively low construction, simple operation/maintenance, and environmental friendliness has been gaining popularity and proposed as alternative treatment approaches of conventional contaminants (i.e. total suspended solids (TSS), biochemical oxygen demand (BOD_5), nitrogen, phosphorus, heavy metals and microbial contaminants) in a variety of wastewaters (Zhi & Ji, 2012). In recent years, due to its distinct advantages, the applicability of CWs has been increasingly explored, and they have proven effective at eliminating not only conventional contaminants but also a wide variety of organic micropollutants including hardly biodegradable organic xenobiotic compounds (i.e. PPCPs) from several types of wastewaters (Zhi & Li, 2012; Zhang *et al.* 2014). The great potential of this low-cost technology of being used for the removal of PPCPs has been proved by different researchers (Li *et al.*

2014; Zhang *et al.* 2014; Verlicchi & Zambello, 2014; Ávila & García, 2015). For instance, Matamoros and Salvado (2012) showed that the use of CWs as tertiary treatment systems resulted, for some PPCPs, in a removal efficiency comparable to advanced treatment systems.

In this context, the objective of this chapter is to overview the current knowledge on the removal of PPCPs from various types of constructed wetlands treating urban wastewaters. The occurrence of the most detected PPCP compounds and the factors affect the performance of the CWs are discussed. Finally, information gaps and questions for future research have been addressed.

5.2 DESIGN AND TYPES OF CONSTRUCTED WETLANDS

Basically, a CW is a small semi-aquatic ecosystem, in which a large population of different microorganism communities proliferates and a variety of physical chemical reactions occur. From technological point of view, CWs are engineered systems that have been designed to take advantage of many of the processes that occur naturally in wetlands, by trying to optimize and speed them up to assist in treating wastewaters (Vymazal, 2005; Wu *et al.* 2015).

CWs differ greatly in design, since a variety of hydrologic modes can be used for their construction (Kadlec & Wallace, 2009). Typically, CWs are classified into three types depending on criteria like hydrology (open water-surface flow and sub-surface flow), type of macrophytic growth (emergent, submerged, free-floating, and floating-leaved) and flow path in wetlands (free water surface (FWS) CWs and subsurface flow (SSF) SSF CWs which could be further divided into vertical flow (VF) and horizontal flow (HF) CWs) (Fonder & Headley, 2013; Valipour & Ahn, 2016). Since in some cases, single-stage CWs may not be able to achieve high removal of PPCPs, two stages combined systems, such as VF–HF CWs, HF–VF CWs, HF-FWS CWs and FWS-HF CWs – known as hybrid CWs – are also applicable for the treatment of wastewater in order to utilize the specific advantages of the different systems (Vymazal, 2005). Furthermore, multi-stage CWs that were comprised of more than three stages CWs were introduced for PPCPs removal in order to realize the improvement of treatment efficiencies (Kadlec & Wallace, 2009; Vymazal, 2014; Ávila & García, 2015).

5.3 REMOVAL MECHANISMS OF PPCPs IN CWs

In aquatic plant-based systems, such as CWs, complex physicochemical and biological processes may occur simultaneously, including sorption, biodegradation, plant uptake, accumulation and translocation as well as hydrolysis and photolysis (Hijosa-Valsero *et al.* 2010a; Verlicchi & Zambello, 2014). Among these processes, the first five are considered to be the major removal mechanisms for PPCPs, whereas the rest can to some extent play a role. In addition, design and operational factors such as loading mode (batch or continuous operational mode), presence of vegetation soil characteristics (e.g., composition of soil organic matter, redox potential, temperature, pH, ionic strength, cations, and anions etc.), depth of bed, plant species, organic and hydraulic loading rate, as well as wetland configuration are also strongly influence PPCP levels and persistence in the wetland environment. Hence, their removal rate can be also correlated with physicochemical parameters, including water solubility, the octanol-water partition coefficient (K_{ow}), dissociation constant (K_a), soil sorption coefficient (K_{oc}) and vapor pressure. For example, it has been demonstrated that hydrophobic PPCPs such as hydrophobic fragrances with high log Kow values (e.g., galaxolide with Log K_{ow} of 4.016 and tonalide with Log K_{ow} of 3.933) may have great potential to be adsorpted in CWs and become more recalcitrant to biodegradation resulting in high accumulation on the medium in wetlands. Similarly, recalcitrant pharmaceuticals such as carbamazepine also have been extensively reported to be removed from the water phase by sorptive effects in CW systems (Matamoros *et al.* 2005, 2008a, b). On the other hand, hydrophilic and moderately hydrophilic PPCPs (with Log K_{ow} ranging from 2.3 to 3) are less susceptible to sorption to sediments or natural organic matter in CWs and are mainly removed by different processes according to the specific physico-chemical characteristics (García *et al.* 2010). Apart from compound's hydrophobic characteristics, weak *van der Waals* and electron donor acceptor interactions for neutral and charged species, respectively, play also a vital role in sorption mechanisms. The conclusion is that sorption mechanisms may hardly be correlated to the value of one parameter (K_{ow}, D_{ow}, K_d) as due to the complexity of the molecule, the fate of a PPCP depends on all of them (Verlicchi & Zambello, 2015).

Besides sorption, biotransformation is another important PPCP removal mechanism in CWs. Despite its importance, however, up to now, there is a lack of data regarding the biotransformation of PPCPs in CWs and only a small number of studies have been published mainly focus on using indirect methods to identify the possible biodegradation pathways for PPCP removal (Onesios *et al.* 2009). Furthermore, the majority of them have been orientated towards the disappearance of the parent compounds and do not investigate the formation of metabolites, which also may be persistent and may have similar ecotoxicological effects. An exception and an interesting example on this subject, is the work of Matamoros *et al.* (2008a) who studied the behavior of two main ibuprofen biotransformation products including carboxy-ibuprofen (CA-IBP) and hydroxy-ibuprofen (OH-IBP) in a HSSF CW system in order to assess the contributions of aerobic and anaerobic pathways to ibuprofen biodegradation. Their findings indicated that both biotransformation products only contributed to 5% of the degraded IBP, demonstrating their negligible accumulation probably due to the similar kinetics for their formation. Similarly, Ávila *et al.* (2013) assessed the removal of various PPCPs and investigated the biotransformation products of these contaminants in SSF CWs. The authors tentatively identified 4-hydroxy-DCF as the metabolite of diclofenac degradation and observed the low values of relative area abundance of 4-hydroxy-DCF with respect to its parent compound (diclofenac).

The uptake of PPCPs by plants is primarily controlled by their bioavailability in the soil-root system. In general, the driving mechanism for uptake and transport of PPCPs within the plant is transpiration (Dodgen *et al.* 2015), and the properties of PPCPs play a vital role during this process (Wu *et al.* 2015). Up to now, factors influencing plant uptake of PPCPs from soil are not well understood and only a few specialized reports are available on this topic. For example, Holling *et al.* (2012) showed that the presence of dissolved organic matter in the planting matrix, might be one of the critical factors determining mobilization and bioavailability of PPCPs soil – plant system. Likewise, in a recent study, Goldstein *et al.* (2014) reported that crops grown in soils with low organic matter and clay contents were at greater risk for uptake and accumulation of PPCPs (Holling *et al.* 2012). In general, due to the lack of investigations, further efforts should be made to reach a final conclusion on the impacts of PPCPs on the soil-plant system.

Following plant uptake, PPCPs may undergo partial or complete degradation, or they may be metabolized or transformed to less toxic compounds and bound in plant tissues in unavailable forms. The extent of distribution within the plant will depend on the compound's physicochemical properties. In general, uptake is greatest for compounds with a Log K_{ow} in the range of 1–4 for non-ionisable compounds. If a compound dissociates in the physiologically relevant pH range, this will influence both uptake velocity and level and octanol water distribution coefficient (Log D_{ow}) which is nearly the same as Log K_{ow} has to be considered instead of Log K_{ow} (Agüera & Lambropoulou, 2016). The uptake and translocation of PPCPs in plants has been documented in several recent studies, proving that many of the PPCP groups such as musks and pharmaceuticals (fluoroquinolones, sulfonamides, tetracyclines, anti-inflammatory and other drugs) are taken up by plants (Wu *et al.* 2015). For example, Eggen *et al.* (2011) demonstrated the uptake of metformin, ciprofloxacin and narasin in carrot (*Daucus carota* ssp. *sativus cvs.* Napoli) and barley (*Hordeum vulgare*), with the root concentration factors (RCF) being higher than the corresponding leaf concentration factors (LCF) for all the target compounds. For all the target plant compartments, the uptake of metformin was higher compared to ciprofloxacin and narasin, indicating a generally higher bioaccumulation pattern in roots (RCF 2–10) and leaves (LCF 0.1–1.5) (Agüera & Lambropoulou, 2016). Finally, recently, Wu *et al.* (2013) compared the accumulation of 20 frequently-occurring PPCPs into four staple vegetables (lettuce, spinach, cucumber, and pepper) grown in nutrient solutions. They found that vegetables were capable of taking up many PPCPs. However, significant disparities in the potential for root uptake and subsequent translocation were observed among the tested compounds. For example, triclocarban, fluoxetine, triclosan, and diazepam accumulated in roots at levels higher than the other PPCPs, whereas translocation to leaves/stems was more extensive for meprobamate, primidone, carbamazepine, dilantin, and diuron.

Similarly to biotransformation, only a few number of studies have been focused on the PPCP photodegradation in aquatic plant-based systems. To the author's knowledge only a few systematic investigations have been conducted for this subject (Llorens *et al.* 2009; Matamoros *et al.* 2008b; Matamoros *et al.* 2012a; Anderson *et al.* 2013). The authors suggested that the sunlight exposure of the water, and therefore photodegradation was the most plausible mechanism for diclofenac and ketoprofen removal in the tested CWs (Llorens *et al.* 2009). Similarly, in a systematic investigation of the role of photodegradation in removing polar microcontaminants in a mesocosm experiment, Matamoros *et al.* (2012a) showed that the concentrations of diclofenac and triclosan declined very fast in all reactors, with the exception of the darkened reactors in which no removal was observed. It was also observed that unplanted control reactors had less mean concentration of diclofenac and triclosan than the reactors planted with *Lemna minor*, since in the latter case the high plant coverage block probably the light radiation and consequently hamper the photodegradation of the tested compounds. Finally, Anderson *et al.* (2013) stated that photodegradation plays an important role in the removal of sulfamethoxazole and sulfapyridine in the tested CWs.

5.4 REMOVAL EFFICIENCIES OF PPCPs IN CONSTRUCTED WETLANDS

The late 2000s and early 2010s would show the first attempts to evaluate CWs with respect to removal of PPCPs from wastewaters (Spain: Matamoros *et al.* 2005, 2006, 2007a, 2008a,b; Portugal: Dordio *et al.* 2007; USA: Conkle *et al.* 2008). After that, many studies have been reported around the world and most of them are recently summarized in comprehensive reviews (Li *et al.* 2014; Zhang *et al.* 2014; Verlicchi & Zambello, 2014). In Table 5.1 some recent CW applications are summarized.

Evaluation of the literature shows that several scales of systems consisting of a single wetland configuration at a time (microcosm, mesocosm, pilot and full-scale systems) have been used for the removal of pharmaceuticals by CWs (Verlicchi & Zambello, 2014). However, studies which evaluate the contribution to PPCP removal of different wetland types within a hybrid system through potential synergies in treatment processes are few (Matamoros & Salvadó, 2012; Ávila *et al.* 2015). The wastewater investigated in the majority of the published studies was urban wastewater (secondary or tertiary effluent) or synthetic urban wastewater. When CWs applied as alternative secondary wastewater treatment systems for the removal of PPCPs, mesocosm-scale systems are usually employed and rarely microcosm- or mesocosm-scale, whereas the opposite is observed when CWs applied as tertiary treatment systems. The most commonly studied pharmaceutical compounds in wastewater were analgesic/anti-inflammatory drugs, antibiotics, beta blockers, antidiabetics, antifungals, hormone inhibitors, diuretics, lipid regulators, psychiatric drugs, stimulants/psychoactive drugs, receptor antagonists and veterinary drugs. Among personal care products, the antimicrobial agents triclosan and triclocarban were the most widely investigated. According to their reported mean removal efficiencies

Table 5.1 Recent applications of CWs as alternative approaches to remove PPCPs from wastewaters.

PPCPs	Matrix	Scale	Type of CWs	Operation of CWs		References
				Types of Plants	Operational Mode HRT (d)	
31 PPCPs: antibiotics, antiepileptics, antiphlogistics (NSAID), antibacterial agents,anticoagulants, beta blockers, contrast mediums, diuretics, fibrates (lipid regulators), pain medicationsand psychoactive drugs (stimulants)	Urban wastewater; Czech Republic	Full scale	HF	*P. australis* *P. australis* + *P. arundinacea*	6.3–11.6	Vymazal *et al.* (2017)
(Ibuprofen, ketoprofen, naproxen, diclofenac, salicylic acid, caffeine, carbamazepine, methyl dihydrojasmonate, galaxolide and tonalide) & 8 of their TPs	Urban wastewater, Spain	Mesocosm-scale	FM; FW; SF; SSF	*Typha angustifolia; Phragmites australis*	29.1–71.1	Hijosa-Valsero *et al.* (2016)
Erythromycin-H_2O; monensin; clarithromycin; leucomycin; sulfamethoxazole; trimethoprim; sulfamethazine and sulfapyridine	Raw domestic Wastewater,China	Mesocosm-scale	SF; HF; VF	*Thalia dealbata Fraser and Iris tectorum Maxim*	20 cm/d*	Chen *et al.* (2016)

Praziquantel	Wastewater from agricultural farm; Czech Republic	Full scale	Hybrid system	*Phragmites australis*	15.7	Marsik *et al.* (2017)
Carbamazepine	Urban wastewater, Mexico	Pilot scale	Hybrid system	*Thypha latifolia, Iris sibirica and Zantedeschia aethiopica*	3	Tejeda *et al.* (2017)
Ibuprofen; diclofenac; acetaminophen; tonalide; oxybenzone; triclosan; bisphenol A, ethinylestradiol	Urban wastewater; Spain	Full scale	Hybrid system	*Mixture of Typha* spp.*, Scirpus* spp.*, Iris pseudacorus, Carex flacca, Cyperus rutundus and Juncus* spp. *w*	<0.5–2.3	Ávila *et al.* (2015)
Enrofloxacin and tetracycline	Livestock industry wastewater.	microcosms	Hybrid system	*Phragmites australis*	7	Fernandes *et al.* (2015)

FM: floating macrophytes, FW: free-water layer; SF: surface flow; SSF: subsurface flow; VF: vertical subsurface flow; HF: horizontal subsurface flow; FWS: free water surface.
*hydraulic loading rates (HLRs).

(Li *et al.* 2014; Zhang *et al.* 2014b; Verlicchi & Zambello, 2014), the PPCPs can be categorized to the readily removed (>70%), moderately removed (between 50% and 70%), low removed (between 20% and 50%), and hardly removed (<20%). Among the readily removed compounds are diclofenac, ibuprofen, ketoprofen, ciprofloxacin, oxytetracycline, nadolol, enrofloxacin, cotinine atenolol and triclosan. Naproxen is moderately removed while the compounds with low removal efficiencies are sulfamethoxazole, clofibric acid, monensin, narasin, salinomycin and carbamazepine. It is worth noting that, for many of the investigated PPCPs, CW systems can offer removal efficiencies as good as conventional WWTPs, and thus it can be proposed as a promising alternative secondary wastewater treatment approach (Li *et al.* 2014; Zhang *et al.* 2014).

5.4.1 Design and operational parameters of CWs on PPCP removal

As previously mentioned, the removal efficiencies of PPCPs in CWs are influenced by several parameters such as influence of plant, seasonality, configuration, operation mode and flow's saturation situation.

Considering the different configurations of CWs, the HSSF CWs, applied separately or associated in hybrid CW system (together with lagoons, ponds, SF-CWs or other HSSF-CWs) have been the most frequently employed aquatic plant-based systems for removal of PPCPs (Zhang *et al.* 2014). In comparison with the SF-CW, the HSSF-CW showed similar removal efficiencies for diclofenac, sulfamethoxazole, clarithromycin and carbamazepine, and lower for ibuprofen and amoxicillin. On the other hand, HSSF-CW was more efficient for the removal of some analgesic/anti-inflammatory (ketoprofen, naproxen, salicylic acid) and antibiotic drugs (sulfadimethoxine, doxycycline, trimethoprim, monensin, narasin and salinomycin). In addition, removal efficiency of HSSF CWs was better for naproxen, diclofenac, carbamazepine, and methyl dihydrojasmonate (83%, 38%, 40%, and 98%, respectively) compared to that of FWS CWs (56%, 0%, 24%, and 82%, respectively) (Hijosa-Valsero *et al.* 2010b).

As regards the VSSF-CWs, although only a very small number of studies have been conducted (Matamoros *et al.* 2007; Matamoros *et al.* 2009a), these systems appear to be more efficient and reliable for the elimination of analgesic/anti-inflammatory drugs (diclofenac, ibuprofen, naproxen and salicylic acid) than the CWs with other configurations; possibly due to their less sensitivity to overloading conditions, shorter HRT and better oxygenation in unsaturated flow. Finally, the hybrid CW systems provide better removal efficiencies for acetaminophen, ibuprofen, naproxen diclofenac and sulfamethoxazole, whereas lower removal efficiencies for salicylic acid, ketoprofen and carbamazepine (Li *et al.* 2014).

Hydraulic load and hydraulic retention time (HRT) are key factors in the success of CWs. In general, the HRT depends on the type of CWs and usually ranged between 1 and 15 days. For example, 1 to 2 days for the VSSF-CWs, 2 to

4 days for the HSSF-CWs, 2 to 6 days for the SF-CWs and 2 to 15 days for the hybrid CWs. Under these different HRT conditions, both batch and continuous operation modes were investigated. Long HRT allows contaminant's extensive interaction with the wastewater. Metcalf and Eddy (1991) reported that the most efficient pollutant removal in CW systems can be accomplished in the range of 4–15 d HRT. Statistical analysis (Pearson correlation analysis) performed by Zhang *et al.* 2014, showed that for ibuprofen, naproxen and diclofenac, a significant ($p < 0.05$) linear correlation existed between pharmaceutical removal efficiency and HRT. On the other hand, carbamazepine and clofibric acid, which have both been classified as recalcitrant compounds in CWS with poor removal efficiencies, were not significantly ($p > 0.05$) correlated to HRT. Despite these expected results, it was somewhat surprising that although salicylic acid was found to be efficiently removed in CWs (Zhang *et al.* 2012a), no linear correlation between removal efficiency and HRT was observed for this compound.

Regarding the vegetation, although the positive role of plants on contaminant removal in CWs has been established, species selection is always one of the important considerations. Plant species differ in terms of growth rates, root morphology, production of root exudates, and oxygen transfer, opening the possibility of microbial community characteristics being specific to plant species. Besides, microbial communities can be very sensitive to exogenous contaminants and can be another important factor affecting the biological degradation behavior of PPCPs in CWs. In this context, plants and microbial communities in CWs are functionally linked and are inherently interdependent with changes in one affecting the other. A number of different macrophyte species have been used for removal of PPCPs in CWs. Among them, the most popular plant species are *Typha* spp. and *Phragmites* spp. However, other species like *Iris sibirica* and *Zantedeschia aethiopica, Juncus effusus, Berula erecta* etc. have been also reported. Meanwhile, the impacts of PPCPs on bacterial communities with different types of plants and microbial removal mechanism in CWs have been poorly investigated (Zhao *et al.* 2015).

The substrate or materials which compose the support matrix, is also important in CWs, since supports the growth of macrophytes and microorganisms and promotes a series of chemical and physical processes. A suitable choice of the latter is especially important for the removal of non-biodegradable PPCP where sorption processes can play the major role in the wastewater treatment. In previous studies, gravel and other materials like stone, lava rock, volcanic rock, zeolite, soil/red soil, sandy soil and sandy clay loam have been proven adequate for the development of plants and microorganisms in CWs and showed a high removal capacity (Li *et al.* 2014; Zhang *et al.* 2014).

5.5 FUTURE GAPS AND RECOMMENDATIONS

The literature reveals that CWs have the potential to contribute to the removal of a wide spectrum of PPCPs from the wastewaters. Despite, however, the rapidly growing knowledge in this topic, up to now information is still insufficient and several issues need further investigations as discussed below:

- Overall, data on the removal efficiencies of the PPCPs for each kind of CWs are scarce. Therefore, further research is needed to enhance our knowledge and attain a more comprehensive picture on their removal among the different types of CWs.
- Considering the fact that current information is limited to a certain number of PPCPs mainly in Europe and North American countries, further work is need to enhance our knowledge on the fate of a wide spectrum of PPCPs in CWs around the world.
- Up to now research have been drawn from experimental systems under controlled conditions. Although lab and pilot-scale trials can provide essential data for modeling the environmental behavior of PPCPs in CWs, due to complexity of the factors influencing their environmental behavior, there is a need for systematic full-scale field applications investigating the role of filling media, plant species, wastewater type, system design and environ-mental parameters on the removal of pharmaceuticals by CWs.
- The majority of the studies were conducted at systems consisting of a single wetland configuration at a time. Therefore, combinations between different CW types belonging to hybrid systems are waiting to be explored in order to gain a further insight in the removal processes.
- To date only a few plants such as *Typha latifolia, Phragmites australis*, have been reported for removal of PPCPs from wastewaters. Therefore, phytoremediation potentials of other wetland plant species, especially those occurring in natural wetlands receiving PPCP contamination, are needed to be tested. Furthermore, the impacts of PPCPs on bacterial communities with different types of plants remain unclear and need to be studied.

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Chapter 6

Heavy metal interactions under the effect of the wastewater and sludge reuse in agriculture

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6.1 THE NEED FOR THE STUDY OF ELEMENTAL INTERACTIONS UNDER THE WASTEWATER AND BIOSOLID REUSE IN AGRICULTURE

The increasing irrigation water shortage in many countries jeopardizes the sustainability of modern agricultural production under xerothermic climates, where irrigated agriculture is extensively practiced. Consequently, alternative irrigation water sources are being sought to supply plants with their water requirements for optimum production.

Treated municipal wastewater (TMWW) is not only an alternative to irrigation water source. Its reuse prevents wastewater disposal into the surface waters such as rivers, lakes, seas, oceans, and minimizes environmental pollution and consequently, more fresh water is economized for domestic and industrial use. Crop irrigation with TMWW provides the additional benefit of nutrients being added to soils during the reuse. In some locations, the TMWW is becoming more attractive because modern wastewater treatment technologies can produce water of good quality.

The TMWW is a carrier of nutrients. For example the average concentration of P and N in the wastewater is 10 and 20 mg/l, respectively. Thus, the application of 1000 m^3 for irrigation may add to the soil 10.0 kg N/ha and 45.8 kg of P_2O_5/ha (Pescod, 1992). In fact, such rates of N and P, not only satisfy crop needs for optimal production, but in some cases may surpass real plant needs. In the long run, significant quantities of nutrients as well as heavy metals may accumulate in the soil and ground water and in some cases at levels that could be toxic to plants.

The annually increasing world population growth requires the intensification and expansion of irrigated agriculture. Therefore, the crop irrigation water needs increase concomitantly in countries with arid and semiarid climates. By necessity, TMWW reuse is becoming a routine agricultural practice, such as in the countries of Near East, China, India Brazil etc (Kalavrouziotis *et al.* 2008). The shortage of irrigation water is intensified by the pressure of the ever growing world population's needs for increased food production under irrigated agriculture. It is estimated that 20×10^6 ha in fifty countries, corresponding to approximately 10% of the total irrigated land, crops are irrigated with raw or semidiluted wastewater (UN World Water Development Report, 2003).

The present work aims at studying the elemental interactions i.e. the synergism and antagonism between heavy metals and macro- and micronutrients, and their impacts on soils and plants under the influence of the TMWW.

6.2 THE WASTEWATER REUSE

The need for an efficient management of the byproducts produced by the modern agricultural, and domestic activities, becomes with the time a "sine qua non" necessity, due to the fact that these byproducts may eventually lead to the pollution of the ecological system with dramatic effects on life of the earth. Since soil is considered an ideal receptor and sink for the removal of such contaminants, land disposal of TMWW is an attractive option. However as the TMWW is a carrier of not only plant nutrients, but also of heavy metals, organic substances, pharmaceuticals and agricultural chemicals, on a long term reuse, these contaminants may accumulate in the soil and via pant growth may enter into the food chain.

6.3 ELEMENTAL INTERACTIONS IN SOIL-PLANT SYSTEM

While the TMWW reuse in agriculture as a source of irrigation water is an attractive option, their heavy metals content may pose serious risk effects, and cause environmental problems, which may be exacerbated by the negative effects of elemental interactions, whose contribution to soils and plants were being ignored for a long time. It is only ten years ago that the World Health Organization (WHO), taking into account our published work on heavy metal interactions (Drakatos *et al.* 2002; Kalavrouziotis & Drakatos, 2002), has included the above published papers as references in the "Guidelines for the safe reuse of wastewater, excreta and grey water" (WHO, 2006).

The elemental interactions, not only among nutrients, and heavy metals, but also with the soil physical, chemical, and biological properties of soils as well, take place continuously within the wastewater, the soils, and the plants. Under the impact of TMWW these interactions may be intensified and increase in number and intensity (Kalavrouziotis *et al.* 2008). The importance of the elemental interactions is based on the fact that they are potentially related to soil fertility, plant productivity and optimum crop growth and yield, and to the environmental quality.

Plants not only take up nutrients, but they also absorb heavy metals during the process of uptake by the roots. These heavy metals do not only contribute to plant growth, but they do interact with each other and continuously change the plant nutritional state and the soil fertility (Kalavrouziotis & Koukoulakis, 2009). During the process of plant nutrient and heavy metal uptake at the root interface and along the transport pathway, the elements interact with each other and compete for bonding sites in the plant (Kalavrouziotis & Koukoulakis, 2009; Marschner, 2002). When the level of one of the interacting elements increases, the other may increase or decrease. In the case of increase, the interaction is synergistic and when it decreases, the interaction is considered antagonistic our knowledge regarding the nature of the elemental interactions is currently limited, and in many cases it is difficult to directly quantify their effects. However, some authors have tried to define these interactions. Thus, synergism between ions is a type of interaction which could be defined as the stimulation of an ion by another one during their uptake by plants (Robson & Pitman, 1983). Similarly, synergism could also be defined as the mutual positive effect of one ion on another in the soil, or at the time of uptake by the plant or during its transfer to the above ground plant organs (Marschner, 2002).

Unfortunately, the mechanism of the synergism is generally not well understood. In fact, only in a few cases an explanation has been given. The effect of synergism on plant growth may be more important quantitatively and qualitatively when the interacting elements in the soil are near the level of deficiency for plant growth (Marschner, 2002). On the other hand, the process of antagonism refers to the competition between essential nutrients or heavy metals occurring in the plants or in soil. Thus, the presence of a given nutrient or heavy metal in high levels may depress the concentration of another nutrient or metal. Such interactions may occur either in soil, or in the root interface or within the plant (Kalavrouziotis & Koukoulakis, 2009). For example, absorption of an element by the root from the soil solution can be affected by another ion in the following ways: (i)- by the decreased or enhanced access to the sites of absorption (ii)- competition at the site of absorption and (iii)- interactions with the metabolic control factors of absorption, such as “ATPase” of an electronic transport system (Robson & Pitman, 1983).

The interactions occurring within the plants may also affect nutrient utilization by impairing the transport of a nutrient to the site of functioning, by enhancing or impairing the nutrients’ function and the site of functioning. The interaction of one nutrient or heavy metal can affect the distribution of another nutrient or metal within the plant by at least three ways: (i)- Impairing the transport of the nutrient or heavy metal by precipitation. (ii)- rendering unable the nutrients for entering into the phloem and immobilizing them in the older leaves thus impairing the re-translocation to the younger leaves. (iii)- modifying the distribution of one nutrient by another within the leaf of the plant (Robson & Pitman, 1983). According to these researchers, interactions related to function may occur: (i)- by the competition of one nutrient with another at the site of function for incorporation into the active sites, (ii)- by the substitution of one nutrient by another, and (iii)- by one nutrient being required for the assimilation or metabolism of another.

Antagonism or competition between elements in plants, is partially explained as occurring during the transfer of ions from the external solution (soil solution) into the cytoplasm where there is a binding at transport sites in the plasma membrane (Marschner, 2002). It is at this location that antagonism between ions with the same electrical charge may occur. The competition is based on "the assumption that the number of binding sites is limited in comparison to the concentration of competing ions, or the limited capacity of the electromagnetic proton pump, or both". This competition occurs between ions with similar physicochemical properties (i.e. valence and diameter) (Marschner, 2002).

The processes which may be related to antagonism between plant nutrients include: (i)- dilution of an element due to the growth promotion by the other interacting element, leading to large biomass production, (ii)- inhibition of nutrient uptake due to cations added in the form of fertilizer, (iii)- P-induced high physiological requirement of an element (e.g. Zn in shoots), and inhibition of elemental translocation from roots to shoots due to physiological inactivation of the element (e.g. Zn) within the roots in the presence of high P levels) (Bolan *et al.* 2005). The processes involved in ion elemental antagonism in the soil are as follows: precipitation, adsorption, and redox potential (Bolan *et al.* 2005; Adriano, 2001). Interactions between ions in the soil occur when the addition of one ion either enhances the precipitation of another element or the dissolution of sparingly soluble compounds (Robson & Pitman, 1983). Some trace elements (cations) can be precipitated in the soil by reacting with anions. The precipitation of Cd, Pb, and Zn as metal phosphates is considered as the main mechanism of their immobilization (Bolan *et al.* 2005). These phosphate compounds are insoluble over a wide pH range, so that precipitation is considered an effective method for ameliorating trace metal in polluted soils. These precipitates are commonly formed as hydroxyl pyromorphites (Adriano, 2001). Precipitation in soil is a process by which metal levels can be controlled. For example, Cd is precipitated as $CdCO_3$ and $Cd(PO_4)_2$, which controls its solubility at high Cd concentrations. It is important to note that Cd precipitation occurs at its higher activities (McBride, 1980).

6.3.1 Factors affecting the interactions

Many factors affect elemental interactions occurring in either soils or plants, such as pH, soil mineralogy, nutrient and metal concentration, plant genotype, etc. Any of these or other unknown factors involved in plant growth, may interfere with the elemental interactions. That is why the interactions are not static, but are always in a dynamic state. Of special importance are those factors which affect the availability of nutrients and heavy metals in the soil. Changes in their levels or intensity, may affect the occurrence of elemental interactions, which are concentration – dependent.

In order for an interaction between two elements to function effectively, the concentration of one of the interacting elements must increase, so that the other can respond positively or negatively.

The changes of interactions are continuous due to the effect of various physical, chemical and plant factors, such as: (i)- soil reaction, ls.(ii)- various inputs applied, such as TMWW reuse, (iii)- clay minerals, (iv)- presence of $CaCO_3$ (v)- organic matter (vi)- plant genotype (vii)- Redox potential (Eh) (viii)- plant growth stage (Rengel & Robinson, 1990).

The adsorption of heavy metals may also affect considerably the occurrence of the elemental interactions. This effect could be more pronounced for the specific adsorption, the reason being the following: two types of adsorption may take place in soil:

(i) Physical adsorption which is due to non-specific electrostatic attraction on the pH-dependent permanent charge of clay surfaces on which sorbed cations can reversibly exchange. This type of adsorption is facilitated by the cation exchange capacity (CEC) of the soil. For example, Cu is adsorbed on the surfaces of silicate clay layers, Fe, Mn, and Al oxides, and organic matter (Adriano, 2001). The fact that the physically adsorbed metals are exchangeable, they can very easily participate in elemental interactions, though not so intensively as the free ions of soil solution.

(ii) Another type of ion adsorption is the "specific adsorption" or also termed "chemisorption" or "surface complexation." Due to bonding on pH dependent variably charged surfaces, the specific adsorption is selective and less reversible than physical adsorption. It may also include complexation with fundamental groups of organic matter. The mineral apatite has been reported to selectively absorb trace metals in an order determined by the pH (Chen *et al.* 1997). It has been reported that Zn, Cd, Sr, Ni and Cu have been found to be sorbed on the surfaces of hydroxyapatite (Misra *et al.* 1975). It can be easily understood that the specifically adsorbed metals cannot participate in the process of elemental interactions, as they are irreversibly being fixed (immobilized). And since the specific adsorption is irreversible, it means that the metals are being fixed. Metals that are fixed are characterized by the lack of chemical activity, contrary to the exchangeable metal forms, which are very active from the chemical and bioavailability point of view Kashem *et al.* (2007). Hence the specific adsorption ca not affect favorably the interactions of metals.

(iii) An additional factor related to the occurrence of interactions is the soil redox potential. The reduction and oxidation reactions refer to the gain or loss of electrons. These reactions take place continuously in soils. Oxidation reactions are related to well drained soils, while reductions, to poorly aerated soils. The soil redox state affects the solubility and hence the availability of some nutrients and heavy metals. For example, Cr, Mn and

Fe are very sensitive metals to the redox potential changes in the soil. One of the main factors that affect the redox state is the change in pH, and soil temperature. For example, Cd remains very soluble in rice paddies under the effect of the drained soil, (high oxidation state) while the CdS remained largely unavailable during the early growth stage of rice when the soil is wet, i.e, high reduction state. On the other hand, Fe and Mn may become unavailable under well drained soil conditions, and therefore they can not compete with Cd, whose plant uptake is increasing (Adriano, 2001).

6.3.2 The study of the elemental Interactions under the treated municipal wastewater

The TMWW, by definition, is considered a "marginal water." Consequently, it requires more complex management practices (Pescod, 1992). This is because its reuse is associated with the human health, and the environmental quality. Therefore, special care must be taken when irrigating crops with TMWW (WHO, 1989). Typically the wastewater consists of 99.9% water with the remaining proportion being soluble solids composed of organic and inorganic compounds, which add considerable amounts of nutrients, and organic matter, as well as a variable amount of heavy metals, (Kalavrouziotis *et al.* 2009; Kabata-Pendias, 2011).

6.3.3 Elemental Interactions occurring in soil and in plants under wastewater

The TMWW is considered a source of nutrient elements and heavy metals (Pescod, 1992), which are added to the soil via reuse. The metals in solution are found in various ionic forms (anions and cations), a large fraction of which is being associated with the organic matter, or found in complex forms, the bioavailability depending on the extent of mineralization of the organic matter, and on the solubility of the metal chelates. The ionic forms are more readily available for interactions (Kalavrouziotis *et al.* 2009). The occurrence of an interaction requires that the concentration of one of the interacting elements be increased gradually, to interact with the other element. The increase of the concentration of the interacting elements in the solution is of great importance for the intensification of the occurrence of elemental interactions (Kalavrouziotis *et al.* 2008).

6.3.3.1 Occurrence of interactions in soil

The heavy metals in the soil, do not interact only between themselves, but also with macro and microelements, and with the soil physical and chemical properties. Therefore, hundreds of interactions occur in the soil affecting positively and negatively the soil fertility and productivity, as well as the growing plant species. Generally, the number of interactions is increasing in the presence of TMWW or of sewage sludge Kalavrouziotis *et al.* (2008). It is estimated that, potentially, at least 392 elemental interactions may occur only in the soil, but not all of them are statistically significant. For example in Table 6.1, the number of various types of statistically significant interactions that were identified at the 1st and 3rd soil sampling, respectively, under the effect of Broccoli, are reported. It is seen that 34 and 40 interactions occurred during the two samplings, respectively, and most of them were synergistic, suggesting that they contributed essential macro and micronutrients and heavy metals to the soil.

Table 6.1 Number of the interactions occurring between macro, micronutrients and heavy metals, in soil, cultivated with Broccoli, during the 1st and 3rd soil sampling[1], under the effect of TMWW. The time difference between the two samplings was 16 weeks (data from Kalavrouziotis *et al.* 2008).

Type of Interactions	**TMWW Total Number of Interactions**	
	1st Soil Sampling	**3rd Soil Sampling**
Synergistic (S)	23	24
Antagonistic (A)	11	3
Syn-Ant. (S-A)	0	1
Ant-Syn. (A-S)	0	12
Total	34	40

1 = 1st sampling corresponds to the commencement of the experiment, and the 3rd to its completion i.e. to harvest.

6.3.3.2 Occurrence of interaction in plants

The response of the plants to the occurrence of interactions under the TMWW, is variable. This conclusion is based on the results obtained from the study of Brussels sprouts plants. (Kalavrouziotis *et al.* 2009) which were as follows (Table 6.2):

(i) Synergistic (S) interactions under TMWW 92.
(ii) Antagonistic (A) interactions under TMWW 62.
(iii) Total number of interactions under the TMWW 177.
(iv) Synergistic interactions under TMWW in the roots were higher than those in the leaves or sprouts i.e. 47 vs 40 vs 5, respectively.
(v) Antagonistic interactions were almost similar in the roots and leaves i.e. 31 vs 30, while only one of them occurred in the sprouts (edible plant part).

Based on the above, it was concluded that the number of interactions taking place in the various plant organs of *Brasica oleracea v*ar gemifera, are generally distributed according to the following order:

Roots > Leaves > Sprouts

The above distribution of the elemental interactions in plants is in line with the general conclusion related to the level of heavy metal accumulation in the various plant organs. That is, the distribution of the heavy metal accumulation seems to be developing in the plant accordingly, i.e higher metal concentration in the roots, lower in the leaves and lowest in the edible plant parts. This conclusion is in line with the results of many workers (NRC, 1996). Examination of the data of Table 6.2 shows that in total only 9 interactions occurred in the edible plant parts, i.e. in the Brussels sprouts under TMWW compared to the total of 177, while 90 of them took place in the roots and 78 in the leaves, It can be seen that most of them are synergistic, having occurred mainly between heavy metals and essential elements. Consequently, these results reflect a minimum accumulation of heavy metals in the edible plant parts.

Table 6.2 Elemental interactions occurring in the Brussels sprouts roots, leaves and sprouts, under the effect of TMWW (data from Kalavrouziotis & Koukoulakis, 2009).

Type of Interaction	TMWW Total Number of Interactions			
	Roots	Leaves	Sprouts	Total
Synergistic (S)	47	40	5	92
Antagonistic (A)	31	30	1	62
S-A	4	5	0	9
A-S	8	3	3	14
Grand total	90	78	9	177

Comparing the total number of interactions occurring under the effect of TMWW in Brussels sprouts, and Broccoli plants (Table 6.3), it is found that most of the total interactions occurred in Brussels sprouts plants, i.e. 177, while in Broccoli only 91. These results suggested that the total number of interaction occurring generally in the plants seems to be species-dependent.

6.3.4 Quantification of elemental contribution by the elemental interactions

The quantification of the interaction's contribution in essential nutrients, and heavy metals, expressed as percent elemental contribution (PEC), was calculated by the method of Kalavrouziotis *et al.* (2010) modified by Koukoulakis *et al.* (2013), This method offers the possibility of quantitatively assessing the elemental contribution of the interactions to soils and plants. The information obtained from such a quantification shows the importance of the elemental contributions of the interactions to plant and soils. This contribution can be positive or negative i.e, increasing or decreasing the concentration of the elements to the extent of creating deficiency symptoms in the plants, which may reduce significantly the plant yields, and in extreme cases, may even lead the plant to death. In Table 6.4 the reported data shows the heavy metals and plant nutrients which have been contributed to Broccoli plants by the elemental interactions. This table reveals that the plant nutrients Mn, Zn, Fe Cu and Ni have been contributed positively to the broccoli heads (edible plant part), while the Cd and Co negatively, with the Pb being contributed statistically non significant. However, the highest contribution of all the metals, except Co, took place in the roots. The percent contribution to leaves was negative in terms of Mn, Zn, Ni and Pb and positive in Fe, Cu, Cd and Co, while in the roots was positive for all metals except for Co which was statistically non significant (Table 6.4).

Table 6.3 Total number of elemental interactions occurring in Brussels sprouts and Broccoli, under the effect of TMWW (data from Kalavrouziotis *et al.* 2009).

Type of Interaction	Vegetable Plant	TMWW
		Total Number of Interactions
Synergistic (S)	Brussels sprouts	95
	Broccoli	43
Anatgonistic (A)	Brussels sprouts	61
	Broccoli	23
S-A	Brussels sprouts	7
	Broccoli	9
A-S	Brussels sprouts	14
	Broccoli	16
Grand total	Brussels sprouts	177
	Broccoli	91

The study of this Table, emphasizes the importance of the elemental contribution by the interactions to soils and plants, and underlines the existence of an additional important natural mechanism for the supply of soils and plants with nutrient elements, in addition to the supply of nutrients by the soil solution or by exchange capacity of soil , which basically provide the plants with available nutrients.

6.3.5 Elemental interactions explaining the positive relation of heavy metals to plant growth

It is well established that generally heavy metals are not considered essential elements and are not needed for plant growth (Adriano, 2001) Yet, at certain times, they have been reported positively involved in plant growth. There have been quite a number of reports stating that at low concentrations some heavy metals influenced favourably plant growth (Bollard, 1983).

So far, this contradictory effect has not satisfactorily been explained. However, the results obtained from our research work in relation to the quantification of the elemental contribution to soils and plants was used to interpret the occasionally reported positive behaviour of some toxic heavy metals in plant growth ,acting as essential nutrient elements (Kalavrouziotis & Koukoulakis, 2011).

Table 6.4 Percent Elemental contribution of interactions between macro, micronutrients and heavy metals to roots, leaves and heads of *Brassica oleracea* var Italica (Broccoli) under the effect of TMWW (data from Kalavrouziotis *et al.* 2009).

Contributed Heavy Metal	Roots	Leaves	Heads
	Percent Elemental Contribution (PEC)		
Mn	67.72	–47.61	81.46
Zn	63.22	–1.10	23.55
Fe	21.06	79.76	72.93
Cu	56.30	5.07	19.05
Cd	37.09	28.57	–64.81
Co	ns	63.52	–99.05
Ni	18.29	–68.00	80.71
Pb	74.64	–38.35	ns

6.4 CONCLUSIONS

Numerous elemental interactions take place in soils and plants under the effect of treated wastewater a large percentage of which, approximately are statistically significant. These interactions have a great impact on soil fertility and productivity of soil and plants. They may either supply the plants or soils with essential plant nutrients and to a smaller extent heavy with metals or may deprive the plants of their plant nutrients to the extent that they may cause nutrient deficiency symptoms. Quantification of the elemental interactions contribution reveals that significant quantities of essential elements or heavy metals ranging from 0–100% of the total bioavailable element are accumulated in the soil or is taken up by plants. It is considered necessary that the interactions due to their importance, be studied thoroughly, and in depth, so as their favorable effects become practically useful.

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Chapter 7

Microplastics and synthetic fibers in treated wastewater and sludge

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7.1 MICROPLASTICS AND SYNTHETIC FIBERS IN THE ENVIRONMENT

In 2009 UNEP published an assessment on the state of the marine environment including socio-economic aspects. In this assessment, the marine debris problem is discussed and a list of both sea-based and land-based sources for marine debris is included. One of the eight main land-based sources listed by UNEP (2009) is identified as "sewage treatment and combined sewer overflows". GESAMP (2010) report discusses UNEP's eight main land-based sources and adds "sewage sludge dumping grounds at sea" as an additional land-based source. This report also suggests that microplastic particles can arise through discharge of macerated wastes, and uses as example of such wastes "sewage sludge" and direct release of micro particles (e.g. scrubs and abrasives in household and personal care products, shot-blasting ship hulls and industrial cleaning products respectively, grinding or milling waste) into waterways and via urban wastewater treatment. It is also suggested that the sources of plastics need to be prioritized, e.g. coastal and land based sources, especially sewage treatment and riverine inputs as well as from shipping. Along with rivers, wastewater discharge is an important point source (Arthur & Baker, 2011) and estimating the contribution of these systems could be the key to quantify inputs. In this chapter, the points of interaction between microplastics and synthetic fibers and a wastewater treatment plant (WWTP), some case studies found in the literature counting the release of such particles to the environment, the implications and possible effective measures to address this problem are presented. Also, the possibility of a WWTP to be the primary source for microplastics is presented.

7.2 DEFINITION OF MICROPLASTICS AND SYNTHETIC FIBERS

Microplastics have been defined as plastic particles, a sub-category of materials called polymers in the size range 1 nm to 5 mm (GESAMP, 2015). In the present study, microplastics are considered as plastic particles with anyone dimension from 5 to 0.3 mm (visible with naked eyes) and synthetic fibers are plastic fibers that are hardly visible with naked eyes. Microplastics can be divided as primary and secondary. Primary microplastics are polymer raw materials and manufactured particles designed for particular applications. A proportion of these particles can be released from discrete point sources such as factories and sewage discharges. Secondary microplastics result from the fragmentation and weathering of larger plastic items.

Microplastic beads in personal care products are the most relevant class of microplastics to wastewater. A study in New Zealand, testing 4 products manufactured in Germany, Korea, France, and Thailand for the microplastics that they contain, found that the microplastics in all brands of facial cleansers show a variety of irregular shapes. Microplastics in the facial cleansers showed a wide size range, with few larger than 1 mm, the majority was smaller than 0.5 mm, and in three out of the four brands the mode was <0.1 mm. In addition to the microplastics, all brands included colored material that most of them did not appear to be constructed from plastic but some were similar in shape to the microplastics (Fendall & Sewell, 2009).

Synthetic fibers such as Nylon©, Orlon©, Dacron©, and Spandex©, are widely used in different applications such as clothing, carpets, upholstery, and other materials. Laundering synthetic textiles releases fibers into sewage systems. Because synthetic fibers are not readily decomposed, they concentrate in sewage sludge and are also discharged in effluents (Habib *et al.* 1998). Experiments sampling wastewater from domestic washing machines demonstrated that a single garment can produce >1900 fibers per wash (Browne *et al.* 2011).

US Clean Water Act aims to limit pollutant discharges to publicly owned treatment works (POTWs) from specific process wastewaters from industrial users. The standards are established based on lists of categories in 40 CFR §. One of the categories, namely 40 CFR §414, includes organic chemicals, plastics, and synthetic fibers (Tchobanoglous *et al.* 2015).

7.3 WWTP

This section describes the points of the WWTP that solid waste can be removed or are relevant. The sources of solids and sludge in a conventional WWTP are as follows (Metcalff & Eddy, 1991): coarse solids from screening, grit and scum from grit removal and preaeration, primary sludge and scum from primary sedimentation, suspended solids from biological treatment, secondary sludge and scum from secondary sedimentation and sludge, compost, and ashes from sludge-processing facilities. Microplastics and synthetic fibers can be found in screenings that include all types of solid wastes, in grit if they are made of plastic that is heavier than water, in scum if they are made of plastic that is lighter than water and it floats, in activated sludge and from chemical precitipation if they are trapped by settling flocculants. Still, microplastics may be captured, if other materials are clogging the screens (Duis & Coors, 2016).

7.3.1 Sewer systems

There are two possible ways for the introduction of microplastics in a WWTP. The direct one is when people are throwing solid wastes to the toilet or the sinks. These if they are large they make clog the pipes otherwise they will be carried through the sewer network to the WWTP along with the wastewater. Some of them may break inside the sewer and thus, their transport will be easier through the pipe network. The indirect introduction of microplastics can happen when the sewer system is carrying both wastewater and stormwater runoff; in other words in combined sewer systems.

Since 1991, combined sewer systems have been identified as problematic since their overflows "can cause adverse receiving water effects including bacteria, nutrients, solids, BOD, metals, and other potentially toxic constituents" (Metcalf & Eddy, 1991). It is obvious from this phrase that microplastics had not been identified as a problem, at that time. Nevertheless, the quality of the stormwater depends both on the atmospheric pollution and on the contaminants of the ground surface that are washed-off. Sewer separation although it was historically considered a good idea, in recent years, it has been reconsidered. The reason is that in a separate sewer system, stormwater runoff is discharged into receiving waters untreated.

The combined sewer overflows can be treated in a separate unit or they can be stored to be treated later during dry weather. Usually they are sent untreated to the receiving waters. The problems associated with the above two options are the cost, the availability of space, and technical issues related to operation of such erratic loading conditions (Metcalf & Eddy, 1991).

7.3.2 WWTP pretreatment

Pretreatment is performed for the removal of constituents that may cause maintenance and operational problems with the rest of the processes of a municipal WWTP (Metcalf & Eddy, 1991). Examples of pretreatment relevant to microplastics include screening and comminution. Screening is the removal of coarse solids by interception; or in other words surface straining. Comminution is the grinding of coarse solids to a more or less uniform size (Metcalf & Eddy, 1991).

Screening is usually the first operation in a WWTP. Bar racks and screens are usually metallic devices with openings of uniform size that let the wastewater pass through but they retain the solid wastes. The design of screening depends of the hydraulic headloss through the screens. Clean screens do not cause significant headloss which however is significantly affected by the method and frequency of cleaning and the size and the amount of solids in the wastewater. The amount of solids collected by the screens can provide an estimate of the solids that can be released to the ocean if there is a stormwater runoff overflow episode or part of the sewer network ends-up in the sea untreated.

7.3.3 WWTP settling tanks

There are WWTPs with both primary and secondary settling tanks. However, in most WWTPs only secondary clarifiers are used to separate activated sludge and treated water. In the second case, it is essential to remove any floating materials so that they do not escape in the receiving water. Usually, the secondary clarifiers are circular with a weir rotating on the water surface. The weir is equipped with scum skimmers and scum baffles that trap scum into a box with a tube that leads the scum out of the settling tank.

7.3.4 Treated wastewater

Treated wastewater is discharged back to the environment usually in a river or stream or directly to a lake, estuary or to the sea. There are regulations related to the suspended solids and the organic loading in the effluent wastewater and in some countries to the coliform bacteria. Also, if the receiver is a sensitive water system then there are regulations related to the nutrients concentrations. Microplastics or synthetic fibers are not regulated and may account for part of the mass of the suspended solids. Treated wastewater may contain microplastic and synthetic fibers if the previous removal technologies are not efficient. In any case, the technologies employed are not designed to remove microplastics or synthetic fibers from the water phase but mainly grit, organic matter, and soap scum.

7.3.5 Sludge

The main body of sludge in a WWTP is produced in the aeration tank and is separated from treated wastewater in the secondary sedimentation tank. It is pumped from the bottom of the tank to other operational facilities that are used for sludge treatment; blending, thickening, stabilization such as aerobic or anaerobic digestion, conditioning, disinfection, etc. Sludge may contain microplastics and synthetic fibers. None of the sludge treatment technologies can remove plastics. Only incineration of sludge could be suitable to destroy plastic.

The presence of synthetic fibers in sewage sludge was initially reported in 1998. These fibers were so abundant that they were proposed as an indicator for the presence of sewage sludge in the soil or in fertilizers (Habib *et al.* 1998). In the dewatered sludge, small pieces of polyethylene and fibers were observed. The fibers occurred in many forms in terms of size, color, and texture. The fibers in sludge products were compared with fibers from common commercial products. Sludge materials contain a variety of textile and paper fibers, including fibers from products such as disposable diapers and sanitary products (Habib *et al.* 1998).

7.4 IMPLICATIONS

Wastewater effluent and sewer overaflow are usually discharged into a surface water body. In addition, untreated sewage is in many regions of the world directly discharged into surface waters. In the developed countries, 80% of wastewater is discharged to WWTPs. However, worldwide only about 15–20% of wastewater is treated (Duis & Coors, 2016). Microplastics from sudge may remain in the soil, be mobilised and distributed by wind, or be transported with surface run-off to the aquatic environment. In most developed countries, ocean disposal of sewage sludge is prohibited. However, in some countries sewage sludge is still disposed at sea and this way, microplastics directly reach the aquatic environment (Duis & Coors, 2016).

Microplastics are distributed throughout the ocean, occurring on shorelines, in surface waters and seabed sediments, from the Arctic to Antarctic (GESAMP, 2015). Microplastics have been found to interact with a wide variety of marine organisms including invertebrates, fish, birds and mammals (Rochman *et al.* 2013). They are known to contain chemicals added during manufacture and can sorb and concentrate contaminants such as pesticides from the surrounding seawater (Ogata *et al.* 2009; Karapanagioti & Klontza, 2008). There is emerging evidence of transfer of chemicals from ingested plastics into tissues. Very small (nano-size) microplastics have been shown to cross cell membranes, under laboratory conditions, causing tissue damage. Ingested microplastics can affect the physiology of the host organism and potentially compromise its fitness (GESAMP, 2015).

Synthetic fibers in treated wastewater are not visible with naked eye and thus, their mass may not be high but the number of these fibers can be really high. High numbers and small size allow these fibers to easily diffuse in the water body that wastewater is discharged. Also, if the WWTP effluent is used for irrigation the synthetic fibers will be spread to the soils. Products such as compost that contain sludge as additive were found to contain fibers. Also, sediments next to sludge treatment plant effluent pipes also contain fibers (Habib *et al.* 1998). Nowadays, plastics are abundant and widespread as macroscopic fragments and virtually ubiquitous as microplastic particles that have been considered by geologists as stratigraphic indicator of the Anthropocene, an epoch of time in which humans have come to dominate many surface geological processes (Zalasiewicz *et al.* 2016).

7.5 CASE STUDIES

Browne *et al.* (2011) were the first to point to WWTP effluents as source for microplastic and especially synthetic fibers and measure them at the WWTP effluents. In two Australian WWTPs with tertiary treatment, the measurements were on average 1 microplastic item per litter of effluent.

Mintenig *et al.* (2014) sampled for microplastics and synthetic fibers in the effluents of 12 WWTPs in Germany. The plastic fiber content of the effluents ranged from 0.1 to 4.8 fibers per litter. The microplastic particles were divided into small (<500 μm) and large (>500 μm) microplastics. Their number ranged from 0.08 to 8.9 small microplastic and from 0 to 0.05 large microplastic particles per litter. Depending on the sewage flow each sewage plant releases from 93 million to 8.2 billion microplastic particles and fibers in the rivers per year. Dubaish and Liebezeit (2013) measured the particles in a German WWTP. They found an average of 33 granules, 24 fragments, and 24 fibers per litter of effluent. Leslie *et al.* (2013) studied the effluent of three Dutch WWTPs that discharge effluents to the North Sea, the Oude Maas River or the North Sea Canal. They found about 52 particles per litter treated effluent. Leslie *et al.* (2012) also studied the removal efficiency in one Dutch WWTP that was 90%. There were about 20 particles per litter in the effluent.

Talvitie and Heinonen (2014) studied the removal efficiency of the central WWTP of St. Petersburg, RU. They observed an average 96% removal for particles and synthetic fibers. In the effluent, 16 for textile fibers, 7 synthetic, and 125 black particles were found per litter. Talvitie *et al.* (2015) also studied the removal of microplastics during different wastewater treatment unit processes in a tertiary WWTP in Helsinki Region, FI. The majority of the fibers were removed in primary sedimentation whereas synthetic particles settled mostly in secondary sedimentation. Biological filtration further improved the removal. In the effluent, an average of 4.9 fibers and 8.6 microplastics were found per litter of wastewater. In the Helsinki archipelago area, the average fiber concentration was 25 times higher and the particle concentration was 3 times higher in the effluent compared to the receiving body of water. This indicates that WWTPs may operate as a route for microplastics entering the sea. Similar observations were made for a WWTP discharging in the River Seine in Paris, FR (Dris *et al.* 2015). The concentration of microplastics in the river water per m^3 was 1000 times less than that in the WWTP effluent.

Carr *et al.* (2016) performed sampling and monitoring at seven tertiary WWTPs and one secondary plant in Southern California, USA. Thousands of litters were filtered using sieves between mesh size 400 and 45 μm. Also millions of litters were skimmed with a device with mesh of 125 μm. In the tertiary plants, microplastics were found to sufficiently being removed during skimming and settling treatment processes. In the effluent of the secondary plant, 1 microplastic was found in every 1140 litters. Although this number seems low and corresponds to a removal efficiency of 99.9%, the daily discharge to aquatic environment is about 100,000 microplastics. The most microplastics were identified to be blue polyethylene microplastics from toothpaste.

Murphy *et al.* (2016) sampled for microplastics at different stages of the treatment process of a secondary WWTP located on the River Clyde, Glasgow, UK. Microplastics were found in sludge, grit, and grease. The removal efficiency was about 98%. In the effluent, 1 microplastic was found in every 4 litters. Despite the large reduction, it was calculated that 65 million microplastics are released from this WWTP into the receiving water every day. A significant proportion of the microplastic was removed during the grease removal stage. This study also shows that despite the efficient removal rates of microplastics achieved by this WWTP when dealing with such a large volume of effluent even a modest amount of microplastics being released per litter of effluent could result in significant amounts of microplastics entering the environment.

Mourgkogiannis (2016) has performed a survey in 101 WWTPs in Greece using questionairres. He found that every day a considerable amount of solid wastes arrive to the WWTP screens. These solid wastes will potentially arrive to the sea in a storm event if the WWTP by pass system is used to avoid flooding. 46% of the operators have observed microplastics in the aeration tank but only 5% observed microplastics in the chlorination tank and 24% in the sludge. 48% of the operators have observed plastics among the floating solids collected in the secondary sedimentation tanks. It is obvious that the mass balance is not correct. This suggest that WWTP operators are not aware to observe and not well-trained to address this problem. The most common solids observed are cotton swabs, bottle caps, other microplastics, and other solid wastes. Cotton swabs were observed floating next to one of this WWTPs and on the adjacent beach (Figure 7.1).

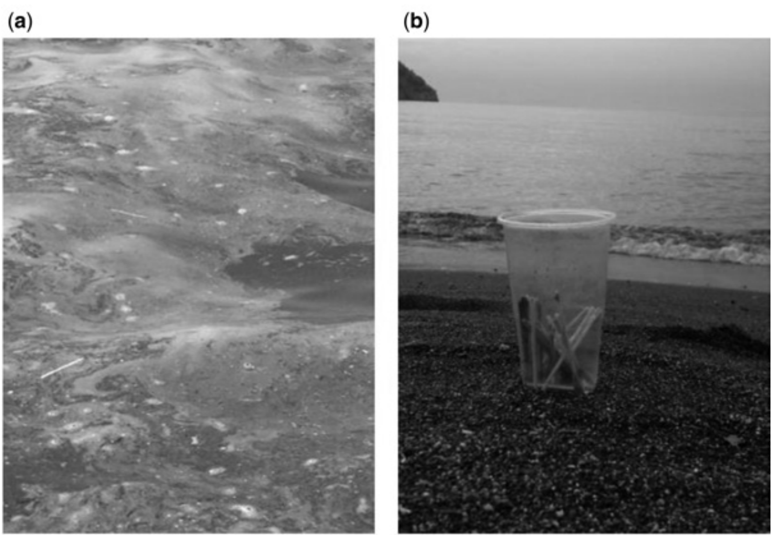

Figure 7.1 Cotton swabs (a) floating on the sea surface next to a WWTP and (b) collected on the adjacent beach of a WWTP.

7.6 EFFECTIVE CONTROL AND TREATMENT SCHEMES

Before discussing treatment schemes for direct microplastic pollution, it is necessary to discuss best management practices for controlling combined sewer overflows. Source controls do not require large capital investments but are common sense practices (Metcalf & Eddy, 1991). The controls relevant to prevent microplastic from stormwater runoff include porous pavements, flow detention, rooftop storage, area drain and roof leader disconnection, utilization of pervious areas for recharge, solid waste management, street sweeping, and public education programs. The physical treatment of combined sewer overflows relevant to microplastics include screens both bar screens and coarse screens and fine screens and microstrainers.

Both consumer decisions and treatment protocols play crucial parts in minimizing microplastic pollution (Chang, 2015). Currently, most WWTPs are ill equipped to handle particulates often too small to sort out. Even in California, WWTPs employ treatment up to the secondary level. In one case only the 4% of the flow is treated through a microfiltration system in its tertiary treatment process with a filter size of 0.1 µm prior to discharge into the San Francisco Bay. This is despite that it is already known that final microfiltration decrease plastic fibers in the effluent and thus, in the sediments adjacent to the discharge pipe (Habib *et al.* 1998). In Germany, the effluent from one WWTP equipped with a final filtration step was sampled before and after filtration. Filtration removed all microplastic particles >500 µm, 93% of the microplastic particles <500 µm, and 98% of the microplastic fibres (Mintenig *et al.* 2004).

Previously, finer screens (23 or 35 µm) are proposed by Metcalff and Eddy (1991) for the removal of residual suspended solids from secondary effluents. This microscreening involves the use of variable low-speed rotating drum filters. The wastewater enters the drum and flows out of the screen cloth. The solids are backwashed toward the highest point of the drum. The solid removal efficiency is about 50% and is sensitive to solids fluctuations. Nowadays, one of the seven measures that can be taken to improve the performance and enhance the reliability of existing and proposed WWTPs is enhanced screening process and possibly fine screening (2 to 6 mm) (Tchobanoglous *et al.* 2015). This is proposed for the removal of inert constituents that can impede treatment performance (e.g., rags and plastic materials).

7.7 WWTPS AS A PRIMARY SOURCE FOR BEACHED MICROPLASTICS

An increasing number of WWTPs is using biocarriers to improve their biological treatment (Gorgun *et al.* 2006; Jenkins & Sanders, 2012). Biocarriers are solid substrates on which microbes are attached instead of being suspended in the aeration tank and are developing biofilms that makes them more resistant to toxic compounds. In our previous studies, we have observed that the bioreactors with biocarriers do not necessarily have better treatment efficiency in the presence of toxic compounds but they are able to support greater abundance of microorganisms in order to perform enhanced biodegradation processes. Moreover the EPS form granules with greater hydrophobicity suggesting enhanced protection of the microorganisms from toxic compounds such as, Cr (VI) and phenanthrene, and better sedimentation ability of the sludge granules (Papadimitriou *et al.* 2010; Sfaelou *et al.* 2015, 2016). The problem is that most WWTP prefer plastic biocarriers than natural media and each plant can use hundreds of thousands to million pieces of biocarriers in its aeration tank.

A foundation (namely Surfrider Foundation Europe), organizing beach cleanups, has observed the existence of plastic biocarriers in several beaches in the Atlantic coast in both France and Spain and also throughout Europe (François Verdet, 2016; personal communication). They have launched a program called "biocarrier watch" that monitors the occurrence of biocarriers in different beaches and produce maps of biocarrier occurrence on their website (https://surfrider64.com/). They have created two reports that list the occurrence of accidental releases of biocarriers from WWTPs. Seven accidental releases of biocarriers have been referenced between 2009 and 2011 in Europe and on the North American continent. Biocarrier leaks due to bad engineering are also possible during regular WWTP operation.

The use of natural biocarrier media is proposed as has been suggested by the food-technology literature (Bekatorou *et al.* 2015; Koutinas *et al.* 2012; Kourkoutas *et al.* 2004) and by novel sorbent literature (Papadimitriou *et al.* 2016). Inorganic and organic materials have been tested successfully such as waste mussel shells, kissiris, and γ-alumina (inorganic) and sawdust, porous delignified cellulose, gluten, spent grains, spent malt rootlets, spent grape skins, and pieces of fruit (organic). The more persistent are the inorganics and sawdust.

7.8 CONCLUSIONS

The main conclusions of the present chapter are as follows:

- Most of the microplastic particles and synthetic fibers can be effectively removed by the different WWTP processes depending on their density. However, more efficient methods such as microfiltration should be employed to protect the environment.
- Despite the high efficient removal rates of microplastics achieved by WWTPs when dealing with such a large volume of effluent even a modest amount of microplastics being released per litter of effluent could result in significant amounts of microplastics entering the environment.
- In most cases, microplastics and synthetic fibers concentration was higher in the WWTP effluent compared to the receiving body of water. This indicates that WWTPs may operate as a route for microplastics entering the sea.

- WWTPs can act as a primary source for beached microplastics.
- WWTP operators should be informed and educated on how to address this issue regulators should prohibit the use of microplastics in personal care products and consumer decision should be based on common sense practices.

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Chapter 8

Wastewater reuse: uptake of contaminants of emerging concern by crops

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8.1 INTRODUCTION

The intensification of agriculture to meet the demand of growing populations is increasing the pressure on natural resources, such as water and land, through high chemical use and intensive soil management (Tilman *et al.* 2002). Extreme climatic events – droughts and floods – are reducing the volume of water available for agriculture. Water scarcity already affects almost every continent and more than 40% of the people on our planet. By 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world's population could be living under water stressed conditions (UN-WATER, 2016). In this context, the reuse of treated wastewater (TWW) can be considered a reliable water supply, quite independent from seasonal drought and weather variability and able to cover peaks in water demand. This can be very beneficial to farming activities that rely on continuous water supply during the irrigation period, consequently reducing the risk of crop failure and income losses. Appropriate consideration for nutrients in TWW could also reduce the use of additional fertilisers resulting in savings for the environment, farmers and wastewater treatment (BIO by Deloitte, 2015). However, TWW usually contains toxic inorganic and organic pollutants and pathogens, which are mostly biologically active and create further potential risk when they enter into the environment or crops used for agricultural irrigation (Becerra-Castro *et al.* 2015; Prosser & Sibley, 2015). Those contaminants, so called contaminants of emerging concern (CECs), are chemicals of a synthetic origin or deriving from a natural source that have been recently discovered to have possible harmful effects on environmental or public health, and to which the extent of such risk are yet to be established (Naidu *et al.* 2016). There are two main routes of exposure to CEC in crops, the use of TWW for water irrigation or the use of biosolids (manure or sludge) as fertilizers (Wu *et al.* 2015). This chapter will be devoted to the crop exposition via irrigation with TWW.

There is major public concern regarding agricultural applications of TWW in the introduction of CECs from irrigation waters to crops via plant uptake as evidenced from a rapid growth in the number of peer-reviewed publications addressing this issue in recent years (Carter *et al.* 2015; Franklin *et al.* 2016; Hurtado *et al.* 2016b; Joseph & Taylor, 2014; Miller *et al.* 2016; Riemenschneider *et al.* 2016). Nevertheless, the risk that accumulated residues may pose to humans via consumption of edible portions is still not well documented (Prosser & Sibley, 2015).

This book chapter will review the most recent studies conducted on the plant uptake of CECs under field conditions irrigated with TWW. Factors affecting the bioavailability-bioaccesibility of CECs by crops, as well as their presence in crops will be evaluated (uptake, translocation, metabolization and accumulation). Finally, both human health implications and some measures to reduce their plant uptake are discussed.

8.2 KEY PHYSICAL-CHEMICAL PROPERTIES OF ORGANIC CONTAMINANTS AFFECTING TO THE UPTAKE

The plant uptake of CECs not only depends on their physicochemical properties (e.g. K_{ow}, pK_a, K_{AW}, and molecular weight), but it also on the physicochemical and biological characteristics of the agricultural soil, which controls the CEC partitioning with soil-pore water (K_d, K_{OC}) or the soil-atmosphere (K_{OA}). Depending on their physicochemical properties, these compounds can be mobilized in aquatic ecosystems, become adsorbed on the soil organic matter, or, if they have certain specific traits (e.g., log Kow, half-life, and molecular weight), be taken up by plants and enter the food chain (Calderón-Preciado *et al.* 2013b). Generally, compounds of intermediate hydrophobicity, log $K_{ow} = 1–3$, are taken up and translocated more easily through the plant compartments than compounds outside this range (Briggs *et al.* 1982). Nevertheless for ionizable CECs, pH-dependent octanol/water partition coefficients (D_{OW}) may be more useful than K_{OW}. D_{OW} is related to the acid–base coefficient (pK_a) of the compound and the medium pH. In a recent study, the accumulation of a suite of 9 CECs was examined in 2 representative eatable crops, lettuce and strawberry. The root concentration factor was found to exhibit a positive linear correlation with the log Dow for the target compounds (Hyland *et al.* 2015b). Similarly, Wu *et al.* (2013) observed that root uptake of neutral CECs was positively correlated with the log D_{ow}, and was likely driven by chemical adsorption into the root surfaces. In contrast, translocation from roots to leaves was negatively related to D_{ow}, suggesting hydrophilicity-regulated transport via xylem. Therefore, for ionizable compounds, the effects of pK_a and pH partitioning are more important than lipophilicity. Generally, dissociation leads to reduced bioaccumulation in plants, but the calculations also predict a high potential for some combinations of environmental and physicochemical properties. Weak acids (pK_a 2–6) may accumulate in leaves and fruits of plants when the soil is acidic. Weak bases (pK_a 6–10) have a very high potential for accumulation when the soil is alkaline (Trapp, 2009). Further description of the effect of pH on the uptake and translocation of CECs is presented in Section 8.4.2. Another relevant physicochemical parameter is the molecular weight of the CECs. In an in-vitro study with spath and lettuce plants, a negative correlation of molecular weight and kinetic uptake rate was found (Calderón-Preciado *et al.* 2012). For instance, only molecules with a molecular weight of less than 500 Da can enter the roots through epidermis of growing root tips, including root hairs by diffusion (Mc Farlane & Trapp, 1994). Nevertheless, plant uptake of compounds with a molecular weight higher than 500 Da has also observed (Blaine *et al.* 2013), probably due to the presence of active transport.

8.3 FACTORS AFFECTING TO BIOAVAILABILITY-BIOACCESIBILITY OF CONTAMINANTS

8.3.1 Water quality

Water quality parameters such as pH and dissolved organic carbon (DOC) can influence the bioaccesibility of contaminants by crops. As stated earlier, the hydrophobic sorption of CEC to organic carbon depend on the form of the chemical in solution and therefore of the pK_a and the pH of the irrigation water. For many CECs, the pK_a is relatively high and outside the normal pH range for, suggesting that pH effects would be minimal. However, for acidic CEC, dissociation of the neutral form to form the organic anion may occur within the normal pH range of wastewater. Electrostatic repulsion between the organic anions and the typically negatively charged clay particle surfaces may result in substantially weaker sorption (Roberts *et al.* 2014). The presence of DOC in the water is important because it can facilitate the movement of CECs within the soils by forming stable DOC-pollutant interactions in solution or by competing with the pollutant molecules for the sorption sites on the soil surface (Graber & Gerstl, 2011). For instance, the DOC's presence significantly reduced sulfapyridine sorption to soil. However, decreasing the solution pH from ~9 to ~6 limited the effect of DOC and revealed the effect of ionic speciation of sulfapyridine (pK_a = 8.4) on the sorption potential (Haham *et al.* 2012).

8.3.2 Soil properties

Soil texture (specific surface area), soil architecture and composition are some of the most relevant factors affecting the behaviour of CECs in soil. For instance, high organic content and clay soil tend to have higher sorption with neutral CECs than sandy and low organic matter content soil. Therefore, soil organic matter (SOM) content increases the sorption capacity of the soil to neutral CEC (Tolls, 2001). For example, it has already been demonstrated that carbamazepine concentration in cucumber fruits and leaves was negatively correlated with SOM content (Shenker *et al.* 2011). Similarly, Goldstein *et al.* (2014) observed that the uptake of neutral CECs exhibited significantly higher concentrations in the leaves of plants (tomatoes and cucumbers) grown in soils containing a low level of SOM and low clay content (i.e., sandy and aeolian soils) as compared to a soil rich in organic matter and clay. Therefore, authors suggested that adsorption of nonionic and polar CECs, such as carbamazepine, sulfapyridine, lamotrigine, and caffeine, through polar interactions with SOM may largely reduce the concentration of these compounds in the soil solution, thus limiting plant uptake. Another important limiting parameter is the biodegradability of CECs in soil, it has been reported that the presence of root exudates can enhance biodegradation of CECs as well as modify the pH near the root surface (1–2 mm) by up to 2 units by secreting H^+, OH^- and organic acids (Carvalho *et al.* 2014; Miller *et al.* 2016).

8.3.3 Climate

Climate conditions such as temperature and humidity are key parameters affecting the bioavailability-bioaccesibility of contaminants by crops. For instance, water solubility and biodegradation kinetics of CECs are higher at greater temperature (Petrie *et al.* 2015), whereas plant transpiration as well as uptake can be higher under higher temperature and low relative humidity ambient conditions. In a recent study (Dodgen *et al.* 2015), carrot, lettuce, and tomato plants were grown in solution containing 16 CECs in either a cool-humid or a warm-dry environment. Leaf bioconcentration factors (BCF) were positively correlated with transpiration for chemical groups of different ionized states ($p < 0.05$). However, root BCFs were correlated with transpiration only for neutral CECs ($p < 0.05$). Neutral and cationic CECs showed similar accumulation, while anionic CEC had significantly higher accumulation in roots and significantly lower accumulation in leaves ($p < 0.05$). Similarly, plants with low transpiration, drought-tolerance, tough cell wall architecture, and tall growth tended to translocate less engineered nanomaterials (Schwab *et al.* 2016).

8.3.4 Irrigation technology

Sprinkler and drip irrigation are commonly used in TWW irrigation. Recent studies and TWW reuse legislation recommend or enforce adopting drip irrigation and suspending watering to prevent environmental and public health hazards when using TWW (Lonigro *et al.* 2016). Regarding the plant uptake of CECs, the use of drip irrigation is more focalized than the sprinkle irrigation. In this sense, Calderon *et al.* (2013a) observed that spraying aqueous solutions of CECs on lettuce leaves yielded to a higher concentration of hydrophobic compounds on the leaf surface.

In this regard, foliar sorption of emerging and priority microcontaminants in leaves wetted by irrigation practices is related to their CEC hydrophobicity (D_{OW}) and volatility (K_{AW}), regardless of their compound class and the relative humidity. Therefore, lipophilic surface of the plant foliage (i.e. cuticle) constitutes an ideal collector for hydrophobic compounds of low volatility characterised by a high K_{OA}. These results underscore the need to improve the quality of reclaimed water in crop irrigation, particularly when sprinkle irrigation is used.

8.4 FATE ORGANIC CONTAMINANTS IN CROPS

The fate of CECs in crops depends on different crops processes, uptake, translocation, metabolization and accumulation in crop plants (Figure 8.1). In the next subsections each of these processes will be discussed.

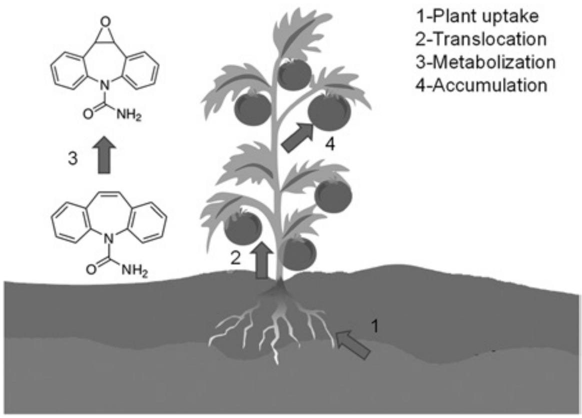

Figure 8.1. Fate of CECs in crops (plant uptake, translocation, metabolization and accumulation). Phase I metabolism of carbamazepine to epoxy-carbamazepine is shown.

8.4.1 Uptake

The uptake of organic contaminants by plants is chiefly controlled by their bioavailability in the soil-root system. Bioavailability is defined as a measure of chemicals' accessibility to plant roots or of their absorbability by living organisms (Reeves, 1998). Usually, plant uptake is measured by the adimensional bioconcentration factor soil-vegetal (BCF_{SV}), which is calculated as the ratio of the concentration of a chemical in the plant tissues to the soil concentration.

Several experiments have been conducted under hydroponic conditions to assess the plant uptake of CECs. In a recent review, Wu *et al.* (2015) pointed out that the BCF values of CECs in roots varied widely. Some CECs such as triclocarban, fluoxetine, diazepam, and triclosan may be highly concentrated in roots, with BCF values up to 111–840 L/kg, while some other CECs such as meprobamate, atorvastatin, diclofenac, and acetaminophen were less concentrated in roots, with BCF values generally less than 5 L/kg. Compared to BCFs obtained from hydroponic studies, BCFs from soil studies (<0.5 to 40 L/kg) were much lower, indicating that interactions between CECs and soil as well as degradation of CECs in soil significantly decreased their bioavailability. Therefore, caution must be taken in extrapolating predictions of plant uptake of PPCPs in real environment based on hydroponic experiments. For example, although fluoxetine was found to highly accumulate in plants grown under hydroponic conditions (Wu *et al.* 2013), it was not found in soybean plants grown in soils irrigated with water containing up to 10 μg/L of fluoxetine(Wu *et al.* 2010), indicating the low bioavailability of fluoxetine in soil, probably due to sorption to soil particles. Furthermore, the BCF strongly depends on plant species and even cultivars (Mattina *et al.* 2006). For instance, Eggen and Lillo (2012) observed that BCF for metformin in rape plants was of 22, whereas it was lower than 0.2 for tomato and squash plants.

To date, very few field studies have been carried out to evaluate the incorporation of waterborne contaminants into crops. Table 8.1 shows that under real field conditions the concentration of CECs in crops depends on climate conditions and their concentration in irrigation waters. For instance, the highest occurrence of CECs in crops was observed in an agricultural field irrigated with river water highly impacted with TWW (concentration of CECs ranging from 80 to 5800 ng/L) and exposed to high temperatures and sun-light radiation (Riemenschneider *et al.* 2016).

Although for most of the CECs such as hormones crop exposure through irrigation with TWW has been found to be more important than the application of biosolids (Shargil *et al.* 2015), it is worth noting that biosolids can also be an important route of exposure for some CECs such as perfluouroalkyl acids (PFAAs). Blaine *et al.* (2013) assessed the plant uptake of PFAAs in a soil amended with industrially contaminated biosolids. They found that BCFs for many perfluoroalkyl acids were well above unity, with perfluorobutanoic acid having the highest BCF in lettuce (57) and perfluoropentanoic acid the highest in tomato (17).

8.4.2 Translocation

Translocation is the transport of materials from leaves or roots to other plant organs. CECs reaching the vascular tissue can be transported to shoots, leaves, and fruit via the xylem (transpiration stream) or phloem (flow of assimilates) (Kvesitadze *et al.* 2016). CECs pass into roots together with water, like nutrients through cuticule-free unsuberized cell walls of young hairs of roots. After penetration, they move towards transport tissue of xylem along free intercellular space (apoplastic way) or cells (symplastic way) (Öztürk *et al.* 2016). Compounds uptaken solely by the

Table 8.1 Concentration of CECs in crops irrigated with treated wastewater.

Country	Water Cource	Water Composition	Irrigation Method	Crop	Crop Concentration	References
USA (Pennsylvania)	WWTP	Sulfomatozaxole (580–22,000 ng/L) Ofloxacin (68–2200 ng/L) Carbamazepine (na-23 ng/L)	Spray-irrigated with WWTP effluent	Wheat plants (Triticum aestivum L.)	Ofloxacin (straw: 10.2 ± 7.05 ng/g; grain (2.28 ± 0.89 ng/g dw) Carbamazepine sulfamethoxazole in grain (1.88 ± 2.11 and 0.64 ± 0.37 ng/g dw, respectively)	Franklin *et al.* (2016)
USA (California)	WWTP	19 EOCs (0.3–181 ng/L)	Overhead sprinklers	Carrot, celery, lettuce, spinach, cabbage, cucumber, bell pepper, tomato	Caffeine, meprobamate, primidone, DEET, carbamazepine, dilantin, naproxen, and triclosan. (0.01–3.87 ng/g dw)	Wu *et al.* (2014)
Jordan	River	28 emerging contaminants (80–5800 ng/L)	Drip irrigation	Cabbage, zucchini, eggplant, tomato, pepper, parsley, rucola, lettuce, carrot, potato	Carbamazepine (up to 216 ng/g dw), and acesulfame (up to 186 ng/g dw) in leaves and caffeine (up to 169 ng/g dw) in roots	Riemenschneider *et al.* (2016)

(*Continued*)

Table 8.1 Concentration of CECs in crops irrigated with treated wastewater (*Continued*).

Country	Water Cource	Water Composition	Irrigation Method	Crop	Crop Concentration	References
Israel	WWTP	Carbamazepine, 10-, 11-epoxycarbamazepine, caffeine, lamotrigine (average concentrations between 0.3–0.82 µg/L)	Lysimeter, Drip irrigation	Carrots and sweet potatoes	0.1–4.1 ng/g fw	Malchi *et al.* (2014)
China	Untreated wastewater and fishpond water	Tetracycline (TC), sulfamethazine (SMZ), norfloxacin (NOR), erythromycin (ERY), and chloramphenicol (CAP) 4–234 ng/L	No avaiable	Cabbage, spinach, radish, corn and rice	NOR (4.6–23.6 µg/kg), CAP (2.6–22.4 µg/kg dw) and TC (4.0–10.1 µg/ kg dw). SMZ and ERY were <LOD	Pan *et al.* (2014)
Spain	WWTP	Caffeine, ibuprofen, naproxen, diclofenac, methyl dihydrojasmonate, tonalide and galaxolide	Drip and sprinkler irrigation	Apple tree leaf and alfalfa	<0.01 to 16.9 ng/g (fw)	Calderón-Preciado *et al.* (2011)

LOD: limit of detection; dw: dry weight; fw: fresh weight.

apoplastic way need to cross the Casparian strip, and for this to happen an active transport must be used (McFarlane & Trapp, 1995).

The translocation of CECs in different plant compartments depends on different physicochemical properties of the soil and chemicals such as the pH, pK_a and K_{OW}. For non ionized hydrophilic compounds, those with log $K_{OW} < 0$ are ambimobile (mobile in both the xylem and phloem) and compounds of intermediate lipophilicity ($0 < \log K_{ow} < 3$) are only xylem-mobile. The highly lipophilic compounds sorb to lipidic membranes and are not readily transported through plants. The mobility of acid compounds depends on their pka and soil pH. When the soil pH is below the inner cell pH (i.e., soil pH 5), and the acidic CECs have a pK_a near soil pH, then the "ion trap" effect occurs: Outside the cell, in soil, the acidic CEC exists as a neutral molecule, and the neutral molecule diffuses passively into the cell. Because the pH inside the cell is above the pH outside, the weak acids dissociate (Trapp, 2004). Acidic CECs with p$K_a < 7$ and log $K_{ow} < 3$ tend to remain in the phloem due to ion-trapping mechanisms and can move to fruits. For bases with p$K_a > 7$, those with log $K_{ow} < 0$ tend to be ambimobile and those with $0 < \log K_{ow} < 4$ tend to move in xylem (Miller *et al.* 2016). For cationic CECs sorption to plant cells walls is expected to be high due to electronegative change of membrane cells, but there is not much information about their translocation into the plant. In addition, some authors have suggested the possibility of using energy-dependent transport mediated by proteins to transport CECs. Many organic nitrogen transporters have low selectivity, suggesting that they could be involved in the uptake of CECs with chemical structures similar to the compounds they transport (Miller *et al.* 2016). LeFevre *et al.* (2015) suggested that the rapid assimilation of benzotriazole by *Arabidopsis* spp in hydroponic systems (approximately 1-log per day) may be due to the tryptophan protein-mediated transport. The antidiabetic metformin with a close structure to guanidine can be also transported through a similar mechanism (Eggen & Lillo, 2012).

The ability of a contaminant to translocate from roots to shoots can be described using the transpiration stream concentration factor (*TSCF*), the ratio of chemical concentration in the xylem pore water to the chemical concentration in the feed solution (Limmer & Burken, 2014). Chemical contaminants with a *TSCF* > 1.0 are actively transported, while chemical contaminants that move in plants at the same rate as water have a *TSCF* near 1.0. For instance, Eggen *et al.* (2013) determined the translocation of 5 organophosphate compounds in barley, wheat, oilseed rape, meadow fescue and four cultivars of carrot grown in pots of agricultural soil. Tris(2-chloroethyl) phosphate (TCEP) (log K_{ow} 1.44) exhibited high translocation to leaves, with leaf concentration factor (*LCF*) ranging from 3.9 in meadow fescue up to 26 and 42 in barley and carrot respectively. For tris(chloroisopropyl) phosphate (log K_{ow} 2.59), *LCF* was high for meadow fescue and carrot (25.9 and 17.5, respectively). Experimental results altogether with simulated models suggested that passive uptake and translocation with the xylem stream are the relevant processes for the high accumulation of these compounds (Trapp & Eggen, 2013).

Carbamazepine (log K_{ow} 2.45) is a well-known example of a CEC that normally occurs at a higher concentration in the aerial tissues than roots (Shenker *et al.* 2011). For instance, Hurtado *et al.* (2016b) found a *TF* of carbamazepine was of 3.4, on average, for lettuce grown under greenhouse controlled conditions.

8.4.3 Metabolization

Most CECs are transformed during a sequential metabolization into more hydrophilic and less toxic compounds. Plants usually detoxify CECs in three consecutive phases (Coleman *et al.* 1997). During phase I metabolism, xenobiotics usually undergo hydroxylation, hydrolysis or other oxidation reactions, producing intermediates with increased polarity or reactivity. Phase II metabolites are the conjugates of parent compound or phase I metabolites with polar biomolecules such as amino acids, glutathione, or carbohydrates (activated xenobiotics). Phase III: compartmentation of conjugated compounds in vacuoles or cell walls. For example, the tonoplast contains ATP-dependent transporters for the compartmentation of glutathione conjugates in vacuoles.

Different studies have focused on the identification of plant metabolites from CECs, but in most of the cases, they were done under hydroponic conditions. Metabolism of diclofenac in *Typha latifolia* included 1 metabolite from phase I (4′-OH-diclofenac) and 2 metabolites from phase II glycoside and glutathione conjugates (4-O-glucopyranosyloxydiclofenac and 4-OH-glutathionyl-diclofenac) (Bartha *et al.* 2014). The formation of epoxy-carbamazepine was observed in lettuce leaves after phase I metabolism of carbamazepine. This is of special relevance because this metabolite is described as being genotoxic (Malchi *et al.* 2014). LeFevre *et al.* (2015) reported aminoacid conjugates and glycosylated metabolites after benzotriazole plant uptake by *Arabidopsis* spp. In addition, in the same study glycosylated bentzotriazole conjugates were observed to be excreted by the plants into the hydroponic medium. Recently, and with the aim of increasing the number of metabolites identified, the use of plant cell cultures instead of the whole plant has been suggested as an excellent model system for the identification of plant metabolites. Cell cultures are not only able to provide novel information on metabolism of selected CECs, but also offer a simple, rapid and inexpensive option (Wu *et al.* 2016).

8.4.4 Accumulation

The bioaccumulation of CECs in agricultural food chains is a process in which pollutants are transferred from contaminated sources, such as ambient air, water and soil to agricultural products, such as crops, and then to humans (Takaki *et al.* 2015).

A recent study investigated how 9 CECs in reclaimed water are taken up into edible portions of two food crops. Two flame retardant chemicals, tris(1-chloro-2-propyl) phosphate (TCPP) and TCEP and several polar pharmaceuticals (carbamazepine, diphenhydramine, sulfamethoxazole, and trimethoprim) accumulated in a linear, concentration-dependent manner in lettuce (*Lactuca sativa*) irrigated with reclaimed water, suggesting passive uptake of both neutral and ionizable chemical contaminants in lettuce. Furthermore, concentration-dependent accumulation of TCEP and TCPP from reclaimed water was also observed in strawberry fruits (*Fragaria ananassa*). Collectively, these data suggest that highly polar or charged contaminants can be taken up by crops from water bearing contaminants of emerging concern and can be accumulated in the edible portions (Hyland *et al.* 2015a).

In addition to the plant uptake from roots, CECs can be accumulated on the surface of the aerial parts of plants. Calderon *et al.* (2013a) observed that the main accumulation pathway for lipophilic CECs in plants is from the water to the leaf surface due to the sprinkler irrigation method. The lipid concentration and surface area of the leaf also influence the degree of accumulation of organic pollutants (Simonich & Hites, 1995).

8.5 HUMAN HEALTH & RISK IMPLICATIONS

The occurrence of CECs in crops could pose a risk to human health, but until now only a few studies have considered their risk in real field conditions. There are two main approaches to assess the human health risk, the use of the acceptable daily intake (ADI) and the threshold of toxicological concern (TTC) level. Proser and Sibley (2015) carried out a risk assessment study of existing iterature reporting the concentration of CECs in edible plants by using ADI approach. They concluded that the majority of individual CECs in the edible tissue of plants due to biosolids or manure amendment or wastewater irrigation represent a minimum risk to human health. Riemenschneider *et al.* (2016) studied 28 CECs (including 9 CBZ metabolites), 10 vegetable species, and 4 plant compartments (roots, shoots, leaves, and fruits). This study used TCC approach and indicated that both the human exposure level as well as the health risk due to consumption of vegetables irrigated with TWW is low (Table 8.2). Nevertheless, authors pointed out that the TTC level of epoxy-carbamazepine and ciprofloxacin would be exceeded for a 70 kg person by the daily consumption of only one potato (100 g/day) or half an eggplant (177 g/day). Similarly, Malchi *et al.* (2014) estimated that the required daily consumption for a child to reach TTC of carrots irrigated with TWW due to the presence of lamotrigine is of 60 g (half-a-carrot). In fact, ciprofloxacin, epoxy-carbamazepine and lamotrigine have been considered as being genotoxic, having a TTC of 2.5 ng/kg body weight per day. Nevertheless, human toxicity should be considered in more detail to clarify the outcome of the structural-alert approach that considers some CECs such as lamotrigine or ciprofloxacin as being potentially genotoxic by using the TCC approach. Regardless of the risk assessment approach used, it is evident that there is a major concern on the undesired intake of CECs within our fresh vegetables. In fact, a recent study carried out by Paltiel *et al.* (2016) demonstrated that in a randomized controlled trial healthy volunteers consuming crops irrigated with TWW excreted carbamazepine and its metabolites in their urine, while subjects consuming fresh water-irrigated produce excreted undetectable or significantly lower levels of carbamazepine.

Table 8.2 Required daily consumption (Kg) by a 70 kg person to reach TTC of crops irrigated with treated municipal wastewater in Jordan. Reprinted with permission from (Riemenschneider *et al.* 2016). Copyright (2016) American Chemical Society.

	a	b	c	d	e	f	g	h	i	j
Carbamazepine (CBZ)	143	39	340	350	211	9.5	9.0	18	8.8	54
EP-CBZ	0.50	0.18	0.55	–	–	0.07	0.04	0.05	0.10	0.16
Trans-DiOH-CBZ	–	90	–	–	–	79	47	–	–	102
3-OH-CBZ	–	–	260	–	–	143	–	237	–	–
Caffeine	66	–	–	–	–	–	–	–	–	–
Gabapentin	–	–	–	–	–	39	–	30	–	75
Ciprofloxacin	0.35	–	–	–	–	–	–	–	–	0.11
Acesulfame	62	–	–	–	–	30	–	–	–	50
Diclofenac	–	70	–	–	–	–	–	–	–	–

a: Cabbage; b: eggplant; c: zucchini; d: Tomato; e: pepper; f: parsley; g: lettuce; h: ruccola; i: potato; j: carrot.

In addition to the occurrence of CECs due to plant uptake, recent studies have revealed significant differences in the concentrations of selected plant hormones (auxins, cytokinins, abscisic acid and jasmonates), and in the nutrient composition of the crops in comparison to crops not exposed to CECs. The exposure of plants to CECs is likely to cause impacts on plant development with unknown implications on human health (Carter *et al.* 2015).

8.6 SOIL AMENDING STRATEGIES

In view of the potential risk that the presence of CECs in crops poses on human health some authors have suggested the use of different soil amending strategies, of which, biochar (BC) is the most studied. The impact of soil amendment with BC to promote soil fertility and for carbon dioxide sequestration has some potential to restrict the bioavailability/bioaccessibility of organic contaminants from irrigation water to plants and thus deserves special attention (Cañameras *et al.* 2016). BC is a solid carbonaceous rich material produced from slow pyrolysis using different feedstocks under a low oxygen atmosphere and at temperatures ranging from 350 to 900°C (Joseph & Taylor, 2014). For instance, Hurtado *et al.* (2016a) found that after 28 days of irrigation with water containing 12 CECs at 15 µg/L (bisphenol A, caffeine, carbamazepine, clofibric acid, furosemide, ibuprofen, methyl dihydrojasmonate, tris(2-chloroethyl) phosphate, triclosan, and tonalide), the average CEC concentration in the roots and leaves of lettuce decreased by 20–76% in biochar amended soil relative to non BC-amended soil. Further studies are needed to characterise the desorption hysteresis effects and the biochar surface biodegradation.

8.7 GENERAL CONCLUSIONS AND RESEARCH NEEDS

The use of TWW for crop irrigation in arid and semi-arid regions is increasing due to climate change. Studies have shown that CECs contained in TWW can accumulate in the tissues of plants. The plant uptake of CECs depends on different physicochemical properties (e.g. K_{OW}, K_{OA}, K_{AW}, pK_a, molecular weight), but is also strongly dependant on the physicochemical and biological characteristics of the agricultural soil (e.g. texture, pH, SOM content). For instance, high organic content and clay soil tend to have higher sorption with CECs than sandy and low organic matter content soil. Climate conditions also play an important role, at higher temperature greater evapotranspiration and plant uptake of CECs has been observed. The use of drip irrigation leads to more restrictive exposure of crops to hydrophobic CECs than the sprinkle irrigation. The fate of CECs in crops depends on different crop processes, uptake, translocation, metabolization and accumulation in crop plants. Plant uptake for neutral compounds is correlated with K_{ow} and for ionisable compounds it depends strongly on the pH of the soil (D_{OW}). Results from real field studies irrigated with TWW concluded that the presence of most of the CECs in crops do not pose a risk to human health. However, toxicological assessment should be addressed in more detail for CECs classified as being genotoxic, since they have been observed to pose a risk to human health. Biochar can be used as soil treatment to attenuate plant uptake of CECs. Nevertheless, it is worth mentioning that the hydroponic food production, or growing crops without soil, is increasing worldwide (Resh & Howard, 2012). Laboratory scale studies have proved that under such conditions the plant uptake of CECs is favoured. Therefore, further studies are necessary to understand the real human health implications of the presence of CECs in such conditions. In this regard, further research needs include: human health risk assessment of the presence of genotoxic substances in crops, the plant uptake of CEC metabolites and their de novo formation in plant. The effects of CECs on plant metabolism, as well as on the formation of endogenous plant compounds that can affect human health, are areas that will require further attention in the future.

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Chapter 9

Bio solids composting and soil applications

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9.1 INTRODUCTION

Biosolids are solid, semi-solid or liquid materials, resulting from treatment of domestic sewage, which has been sufficiently processed to be used for land-application. The term was introduced by the wastewater treatment industry in the early 1990's and has been recently adopted by the United States Environmental Protection Agency (U.S. EPA) to distinguish high quality, treated sewage sludge from raw sewage sludge and from sewage sludge containing large amounts of pollutants (Evanylo, 2009). Moreover biosolids is used to describe the material after it has been stabilized in the digestion process. Stabilization decomposes the solids, reduces odours and destroys most of the bacteria in the material. At the end of the digestion process, the biosolids meet safety and beneficial recycling criteria. Mateo-Sagasta *et al.* (2010) mentioned that a properly treated, sewage sludge is called biosolids and if it's safe can be marketed for beneficial uses e.g. in landscaping. On the other hand according to Zorpas (2012a) sewage sludge is a wastewater industrial sub-product with high organic matter and nutritional contents traditionally used as an agricultural soil fertilizer (after composting).

9.2 BIOSOLIDS REGULATION

Several Directives have an influence on sludge management but the most significant are the Directives 2000/60/EC on water protection (Water Framework Directive: WFD), 91/271/EEC on urban waste water treatment (WWT), 99/31/EC on the

Landfill of Waste and 86/278/EEC on the use of sludge in agriculture. In particular, the WFD targets the long-term progressive reduction of contaminant discharges to the aquatic environment in urban wastewater while the Directive 91/271/EEC, concerns urban WWT and aims the protection of the water environment from the adverse effects of discharges of urban waste water and from certain industrial discharges (European Commission, 2001; Inglezakis *et al.* 2014; European Commission website, 2016). Directive 91/271/EEC seeks to encourage the use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects on soil, vegetation, animals and man. In particular, the Article 14 the 91/271/EEC states that "Sludge arising from waste water treatment shall be re-used whenever appropriate. Disposal routes shall minimise the adverse effects on the environment." Furthermore, the EC Directive 99/31/EC on the Landfill of Waste also impacts on the disposal of sewage sludge particularly with the stringent new standards relating to landfill of biodegradable waste (target for the reduction of biodegradable waste to landfill is to 35% by 2016). Moreover, according to Kelessidis and Stasinakis (2012) the main legislative text that refers to sludge management is the Directive 86/278/EEC on the use of sludge in agriculture. This 86/278/EEC seeks to encourage safe use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects on soil, vegetation, animals and humans. Among others, it specifies rules for the sampling and analysis of sludge and soils, sets out record keeping requirements and limit values for concentrations of heavy metals in sewage sludge and soil (Table 9.1).

Table 9.1 Annexes IA, IB and IC of directive 86/278/EEC.

Metal	Limit Values for Concentrations of Heavy Metals in Soil (mg/kg dm), for 6 < pH < 7	Limit Values for Heavy Metal Concentrations in Sludge for Use in Agriculture (mg/kg dm)	Limit Values of Heavy Metals which may be Added Annually to Agricultural Land, Based on a 10 Year Average (kg/ha/y)
Cadmium	1–3	20–40	0.15
Copper	50–140	1000–1750	12
Mercury	1–1.5	16–25	0.1
Nickel	30–75	300–400	3
Lead	50–300	750–1200	15
Zinc	150–300	2500–4000	30

In USA according to (EPA, 1999) biosolids must meet the requirements specified in the 40 CFR Part 503 Biosolids Rule, "The Standards for the Use or Disposal of Sewage Sludge" before they can be beneficially used. The Part

503 Biosolids Rule land application requirements ensure that any biosolids that are land applied contain pathogens and metals that are below specified levels to protect the health of humans, animals, and plants. The Part 503 Biosolids Rule divides biosolids into “Class A” and “Class B” in terms of pathogen levels. Class A biosolids must undergo treatment that reduces pathogens (including pathogenic bacteria, enteric viruses and viable helminth ova) in the biosolids below detectable levels. Class A biosolids (but not Class B) can be used as bagged biosolids marketed to the public. Class B biosolids ensure that pathogens in biosolids have been reduced to levels that are protective of public health and the environment under the specific use conditions. Class B biosolids cannot be sold or given away in a bag or other container for land application at public contact sites, lawns, and home gardens. Class B biosolids can be used in bulk at appropriate types of land application sites, such as agricultural lands, forests, and reclamation sites, if the biosolids meet the limits on metals, vector attraction reduction, and other management requirements of Part 503. Biosolids can be used as MSW landfill cover, as long as they meet regulatory requirements in 40 CFR Part 258, which governs MSW landfills.

9.3 CHARACTERISTICS OF BIOSOLIDS

Before the final application of biosolids in land, several biological, chemical (are great important), and physical analyses must be done. Solid concentration is perhaps the most important variable in defining the volume of sludge to be handled and determining whether the sludge behaves as a liquid or a solid. The specific gravity of inorganic solids is about 2–2.5 and that of the organic fraction is 1.2–1.3 (Al-Malack & Rahman, 2012). Rheological characteristics of sludge are very important because they are one of only few truly basic parameters describing the physical nature of sludge. Sludge varies from a Newtonian fluid, where shear is proportional to the velocity gradient, to a plastic fluid, where a threshold shear must be reached before the sludge starts to move. Most wastewater sludges are pseudoplastic. Some of the most important parameters are (Evanylo, 2009; Zorpas, 2012a,b; Al-Malack & Rahman, 2012):

- *Total solids (TS)*: TS include suspended (SS) and dissolved solids (DS) and are usually expressed as the concentration present in biosolids and depend on the type of wastewater process and biosolids’ treatment prior to land application. Typical solids contents of various biosolids’ processes are: liquid (2–12%), dewatered (12–30%), and dried or composted (50%).
- *Volatile solids (VS)*: VS provide an estimate of the readily decomposable organic matter in biosolids and are usually expressed as a percentage of TS. Several treatment processes, including anaerobic digestion, aerobic digestion, alkaline stabilization, and composting, can be used to reduce VS content and the potential for odor.

- pH is the degree of acidity or alkalinity of a substance. Biosolids pH is often raised with alkaline materials to reduce pathogen content and attraction of disease-spreading organisms (vectors). pH > 11 kills virtually all pathogens and reduces the solubility, biological availability and mobility of most metals.
- Lime also increases the gaseous loss (volatilization) of the ammonia (NH_3) form of nitrogen (N), thus reducing the N-fertilizer value of biosolids.
- Pathogens, are parasites (microorganisms) in the wide sense of the word and in the general case they are disease-causing (Biosolids Applied to Land, 2002) and can present a public health hazard if they are transferred to food crops grown on land to which biosolids are applied. The most important pathogens which can be identified in municipal wastewaters and solids are (i) Bacteria like *Salmonella sp, Escharichia coli, Shigella sp,* (ii) Enteric Viruses like *Hepatitis A virus* and *Echoviruses*, (iii) Protozoa like *Entamoeba histolytica* and *Giardia lamblia*, (iv) Helminth warms like *Ascaris sp., Trichuris trichiura, Toxocara canis*, etc.
- Nutrients are elements required for plant growth that provide biosolids with most of their economic value. These include nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), sulfur (S), boron (B), ammonia (NH_4). Concentrations can vary significantly and when bio solids are being considered for land application should be analysed.
- The trace elements of interest in biosolids are those commonly referred to as "heavy metals." Some of these trace elements (e.g., Cu, Mo, Zn) are nutrients needed for plant growth in low concentrations, but all of these elements can be toxic to humans, animals or plants at high concentrations. Several studies (Zorpas *et al.* 2011; Zorpas, 2011, 2014) have shown that the main urban wastewater pollution sources of potentially toxic elements (such as Zn, Cu, Ni, Cd, Pb, Cr, Hg, As, Mo etc) are from industrial point sources and thus, metal concentrations in sewage sludge mainly depend on the type and amount of industrial waste discharged into system. Because metals are generally insoluble they usually present at higher levels in sewage sludge than in wastewater and dewatering of sewage sludge has a minimal impact on reducing metal concentrations (Process Design Manual, 1995).
- Phytotoxicity has been associated with immaturity of compost and depletion of organic acids. For compost to be used not for mulching but for row or container crops, its high stability or maturity is desirable as instable or immature compost is often odorous and phytotoxic, and interfere with seed germination index (GI) due to the elevated concentration of NH_3, salt content, organic acids etc. Zorpas (2008, 2009) mentioned that, if the $0 < GI < 26$ the substrate is characterized as very phytotoxic, $27 < GI < 66$ the substrate is characterized as phytotoxic, $67 < GI < 100$ the substrate is characterized as non-phytotoxic and if the $GI > 101$ then the substrate is characterized as phyto-nutrient.

9.4 APPLICATIONS OF BIOSOLIDS

The main potential uses for biosolids (Vasileski, 2007) are (i) the Agricultural land application as fertilizer/soil conditioner for human crops production and for animal crops production (ii) Non-agricultural land application for forest crops (land restoration, forestry), land reclamation-renovation (roads, urban wetlands), reclaiming mining sites and landscaping (recreation fields and domestic use), (iii) energy recovery and energy production for heat generation (through incineration or gasification) and for oil and the production of cement and (iv) for commercial uses. Land application according to Zorpas (2008) is consider to be one of the important alternatives. The use of biosolids for fertilizer or soil conditioner for human crops production is an age old practice prior the investigation of chemical fertilizers (Vasileski, 2007) in order to increase crop production. Biosolids application to agricultural land has been used for a number of years.

Landfilling disposal (Evanylo, 2009) provide the simplest solution to biosolids handling by concentrating the material in a single location. The risk of release of biosolids-borne pollutants and pathogens is minimal if the landfill is properly constructed and maintained. Economically, the cost compares favorably with other options. Landfill disposal is not, however, without risks. Buried organic wastes undergo anaerobic decomposition which produces methane gas. The chemicals and nutrients including heavy metals if exist can pose risk to local groundwater from older landfills that do not have synthetic liners or from a liner in a newer landfill developing a leak. In addition, the potential benefits of the organic matter and plant nutrients in the biosolids are lost with landfilling. Wastewater spreading on soil, also known as "land treatment", has a long history, as demonstrated by the elaborate sewerage systems associated with ancient palaces and cities of the Minoan Civilization, approximately 4000 years ago (Angelakis *et al.* 2005). Nowadays, wastewater management is extremely importance in order to meet future water demands, and ta the same time to prevent environmental degradation and to ensure sustainable growth, as is expected to increase the use of advanced wastewater management and the use of sewage biosolids (Paranychianakis *et al.* 2006). In the industrial world, more than one-half of biosolids produced in the USA (Lyberatos *et al.* 2011) and about 40% of that produced in the EU countries (Table 9.2) (WRc, Milieu, Ltd. & RPA, 2008) is recycled to land. Land application of biosolids is usually less expensive than alternative methods of disposal. Consequently, wastewater treatment facilities and the public they serve benefit through cost savings. The recycling of nutrients and organic matter can be attractive to citizens concerned with environmental protection and resource conservation.

Land application of sewage sludge has been extensively used as an effective dispersive method throughout Canada, the United States and Europe for more than 40 years. Many studies have demonstrated the positive effect of land application of sewage sludge or sludge compost on corn and forage yields and soils (Tiffany *et al.* 2000; Zorpas, 2012a). In the few instances where a nil or negative response to these organic amendments have been observed, either a high C:N ratio, excess metals, high soluble salts or extremely high application rates were responsible for the reduced yields or negative effects to soils or crops. The primary plant nutrient associated with sewage sludge is N; however, sludges also contribute significant amounts of other macro and micronutrients (Zorpas, 2009). Nitrogen availability from sewage sludge and sludge compost is reported to range from 0% to 56% (Zorpas, 2012b). Excessive applications of sewage sludge beyond crop requirements and the soils absorptive capacity or applications made in the fall or winter may result in groundwater contamination by nitrates, loss of N through denitrification, toxic nitrate concentrations in animals (especially from grass forages), and surface water contamination by P.

China (LeBlanc *et al.* 2008) is one of the fastest-growing economies in the world, with a high rate of technological development. China reports a one-year increase in sewage production in the country's urban areas of 5.4%. Wastewater sludge management is overseen by national ministries, and new regulations were released in 2007 that set standards for the levels of contaminants in wastewater sludges and the options of use and disposal: "four types: land application, landfill, production of usable materials and incineration." China, like other middle-income countries, is in the midst of updating and strengthening its wastewater sludge management program. China is leap-frogging to an advanced regulatory program that includes encouragements for biosolids recycling to soils, restrictions on use on food crops and grazing lands, limits on heavy metals and dioxins and furans reflective of those in the USA and EU, and concerns about persistent organic pollutants and endocrine disrupters. Land application of biosolids in agricultural settings is the most common use or disposal in China. Russia (LeBlanc *et al.* 2008) shares many of the same challenges as China, except for the population pressures. Some of its wastewater treatment infrastructure is 50 years old or more, and Russia has considerable experience with wastewater sludge management. However, it took is strengthening its regulations and working to ensure proper management and best practices are in force. In Brazil and Mexico (LeBlanc *et al.* 2008), research is advancing the use of biosolids on land, and, in both countries, demonstration projects are showing the value and controllable risks of this method for managing wastewater solids. In Brazil, there are restrictions on slope (>5%), the kinds of crops biosolids can be used on, and the time of year when applications to land can be done, to avoid excessive runoff in the rainy season. It is common for agricultural soils throughout much of Australia, and particularly Western Australian (LeBlanc *et al.* 2008) to suffer from nutrient deficiencies and/or soil acidity. Direct land application of biosolids has shown marked improvements in soils and crop production when applied in these areas, which is reflected by the high demand for biosolids in the agricultural regions. Biosolids are applied to land utilising tractor-drawn manure spreaders. Application rates are calculated by determining the contaminant loading, nutrient loading and plant nutrient requirement with the lesser value determining the final application rate. Perth metropolitan biosolids are applied at either plant nutrient requirement (N) for broad acre crops such as canola, wheat, oats (for dewatered cake) or soil pH requirement (for lime amended biosolids). The application rate for nitrogen assumes that 15% of the total nitrogen is mineralised whilst phosphorus is assumed to have 21% available P to the plant. Biosolids dewatered cake is currently applied at rates of 8 dry t/ha. Biosolids applications are usually followed by incorporation into the soil within 36 hours.

Table 9.2 Generation of sewage biosolids most managed methods in EU.

Countries	Total Volume (t Dry Solid/y)	Land Use %	Landfill %	Incineration %	Other %
Austria	266100	18	12	48	22
Bulgaria	29987	40			
Belgium	136260				
Brussels	2967	0	55	10	45
Finland	101913	0	9	34	7
Cyprus	7586	41	50		9
Czech Republic	231000	26	60		14
Denmark	140021	59	61	6	10
Finland	147000	3	40	2	55
France	1125000	70	5	25	
Germany	2056486	29	10	21	40
Greece	167289	3	96	0	1
Hungary	128380	26			
Ireland	42147	63	37	0	
Italy	1070080	18	28	2	52
Latvia	23942	37			
Lithuania	76450	32			
Luxemburg	7750	43	42	0	15
Poland	523674	17			
Portugal	408710	46	40		14
Roumania	137145	0			
Slovakia	54780	0			
Slovenia	21139	0			
Spain	1064972	65	25	10	
Sweden	210000	14	42	5	39
Nederlands	550000	0	0	58	28
UK	1544919	68	32		
Malts	No data available				

Incineration (Evanylo, 2009) reduces biosolids volume, kills pathogens, destroys most of the organic chemicals, and provides energy. The remaining ash is a stable, relatively inert, inorganic material that possesses 10 to 20% of the original volume. Trace elements are not destroyed during incineration, which increases their concentrations in the ash by five to ten-folds. Incineration releases CO_2 (another green house gas) and is one of the more expensive options for biosolids disposal because it requires sophisticated systems to remove fine particulate matter (fly ash) and volatile pollutants from stack gases. Furthermore, the ash containing the higher trace element concentrations must usually be landfilled. As with landfilling, the potential benefits of organic matter and plant nutrient recycling are lost. Naoum *et al.* (1999) and Zorpas *et al.* (2001) study the impact of thermal treatment on sewage sludge. According to both researchers for the thermal treatment of sludge, knowledge of the salt and heavy metal content is important for the choice of the right flue gas cleaning system. The advantage of thermal sludge treatment as opposed to dumping and utilization systems must be seen in the thermal destruction of the organic pollutants. At the same time, a large part of the heavy metals is evaporated by the high burning temperature. Moreover Zorpas *et al.* (2001) mentioned that the thermal treatment of sewage sludge up to 900°C, resulted in a mass reduction of approximately 84%. The mass reduction (Figure 9.1) observed when dried (at 105°C) samples are subjected to thermal treatment up to 900°C was 56.4% while 45.0% when samples are treated up to 650°C.

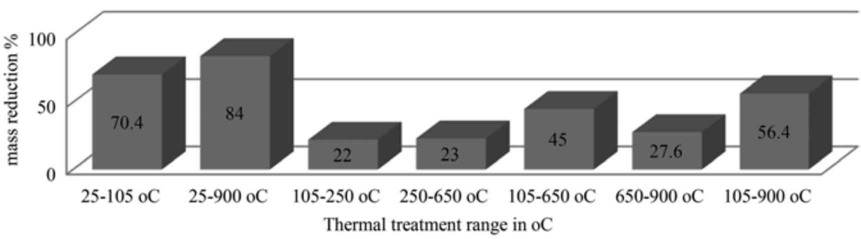

Figure 9.1 Mass reduction (%) of the sludge due to thermal treatment.

9.5 COMPOSTING

For the Biosolids compost the most important characteristics are the concentrations of pathogens, the presents of the heavy metals, the soluble salts, the odor, the stability, the pH, phytotoxicity and particle size. In contrast to biosolids the MSW compost has different characteristics. Those involves pathogens, the present of heavy metals, the soluble salts, the concentration of boron, the stability, the odor, the maturity, the pH, the EC, the inert (plastic, metals, glass), the humics, and the particle size. On the other the most important characteristics from yard waste compost are the stability maturity, odor, pH and houmus. Also the compost produces from sewage sludge present similar characteristics with the other compost but among the most important characteristics are the present of heavy metals, the chemical extraction of metals, the metals leachability, the houmics, the pH and the Electronic Conductivity, the pathogens, the phytotoxicity, the maturity and the stability (Zorpas, 2009; Zorpas, 2012a,b). Composting provides a simple and a cost effective alternative treatment method for sewage sludge by decomposing organic matter, producing a stabilized residue and disinfecting pathogens (Zorpas *et al.* 1999). The composted product can also be used as a fertilizer or soil conditioner because of its large content of stabilized organic matter. However, the high content of heavy metals in sewage sludge compost has proven to be a limiting factor in the land application of sewage sludge compost (Wong *et al.* 1999). The sludge is classified as solid waste that requires special methods of disposal, because of its noxious properties. However, much of the sludge originating from urban wastewater treatment is contaminated with heavy metals (Sims & Skline, 1991; Garcia-Delgado *et al.* 1994; Zorpas *et al.* 1998). Theses metals, may leach from sludge and enter the ecosystem, the food chain and finally the human body. Zeolites may be useful as metal scavengers in metal-rich sludges. Natural zeolites such as Clinoptilolite (Cli) have the ability to take-up and remove these metals by utilizing ion exchange. The addition of natural zeolite, clinoptilolite, during sewage sludge composting has been proven to be a promising way to reduce the heavy metals content (Zorpas *et al.* 2000, 2003), since zeolite (clinoptilolite), has the ability to take up heavy metals. Zeolite utilization has become popular in the last decade, due to its cation exchange and molecular sieving properties (Zorpas *et al.* 2009; Zorpas, 2012b). Also, total concentration of heavy metals cannot provide useful information about the risk of bioavailability, toxicity and capacity for remobilization of heavy metals in environment (Zorpas *et al.* 2008) but the chemical fraction of the metals indicated which of those are associated with the mobile fractions (exchangeable, carbonates) and les mobile form (organic and residual fraction) (Zorpas *et al.* 2008).

Sewage biosolis can be used to improve the quality of compost with low potassium content by mixing and co-composting with cow manure of high potassium content and/or other fermentable solid waste sources, such as crop residues or municipal solid wastes, green or wood processing wastes etc., leading to the production of high quality “fused” compost. Utilization of compost in crop management provides considerable advantages, as it reduces the input of expensive chemically-synthesised nitrogen and phosphorus fertilizers and contributes to prevent land degradation. During the composting process of sludge from wastewaters microbiological stabilization, partial dehydration and enrichment in nutrient content occur (Zorpas, 2009). Nevertheless, depending on the conditions during this process, sewage sludge might contain pathogenic microorganisms (e.g., Salmonellas and enteroviruses) (Zorpas, 2009) and heavy metals that can affect both soil pollution (Zorpas, 2011) and the uptake of these metals by roots, especially in horticultural crops or using natural zeolites (Zorpas *et al.* 2008;

Zorpas, 2008). Many publications have already stated some beneficial effects of the application of composted sewage sludge from wastewater to several kinds of soils, including agricultural soils, under different weather conditions and using compost from different sources highly variable in nutritional composition (Zorpas, 2009; Hamidpour, 2012). The addition of compost to disturbed soils improves the soil physical characteristics, including water holding capacity, bulk density and aggregation (LeBlanc *et al.* 2008).

9.6 BIOSOLIDS IMPACT ASSESSMENT

The disposal of sludge always requires very positive and careful management but the ease, or difficulty, with which disposal is actually achieved, and the associated costs depend very much on circumstances. Local and national geographical, agronomic, economic and stakeholder perception factors have considerable influence. The management of sewage sludge in an economically and environmentally acceptable way is a matter of increasing importance. The leaching of nutrients (nitrogen and phosphorus), metals or organic substances from biosolids into groundwater is an issue of potential concern. In Europe concern over the potential effects on human health due to increased concentrations of nitrate in water supplies has resulted in regulatory action to control the application to agricultural land of all nitrogen (N) sources, including sewage sludge (Council of the European Communities, 1991). Biosolids generally have low N content (1–6%) relative to nitrogenous fertilisers. Relative to raw sewage, the organic matter in biosolids (compost in particular) is highly stabilised, and even high rates of application pose little risk of nitrate leaching (Smith, 1996). Only a small proportion (approximately 10%) of the total N applied is available on an annual basis. The mineralisation of organic N in sewage sludge takes place quite slowly relative to N in other wastes (e.g., poultry litter, pig effluent). Sewage sludge contains a great variety of human pathogenic organisms which originate directly from the excreta of man or animals, or which have multiplied in the wastewater during transport to the treatment plant. Use of sludges in agriculture may therefore create risks to the health of man or animals. These health risks may be rather direct as through the consumption of contaminated crops, or indirect as through the contamination of food animals which may become healthy carriers of pathogenic agents. A study from Sweden (Sahlstrom *et al.* 2004) surveyed the presence of bacterial pathogens (*Salmonella, Listeria, Campylobacter, E coli*) in eight Swedish sewage treatment plants. Listeria is an important human and exist in sewage sludge according to De Luca *et al.* (1998). A major environmental impact nowadays is the pharmaceuticals (Zorpas *et al.* 2012). A huge range of drugs (Anti-inflammatory drugs and analgesics: antibiotics, aspirins, Sulphasalazine, Dextropropoxyphene etc) both prescribed and over-the-counter medications are taken daily and those which are excreted unchanged will appear in sewage sludge along with the break down products of those which the body metabolizes. In terms of risk, there are no data for levels of these drugs in sewage to be able to estimate such risks. Historically sludge and/or trace metal application limits were developed on the basis of phytotoxicity but more recently these were lowered to take into account the possibility of accumulation in the food chain (Zorpas, 2012a,b). High levels of trace metals applied to land with sludge can lead to increased concentrations in vegetation (Chang *et al.* 1987). Cadmium presents a significant risk to human health (Chang *et al.* 1987) and accumulates in many plants such as soyabeans (Heckman *et al.* 1987), wheat (Lubben & Sauerbeck, 1989) corn (Rappaport *et al.* 1988) and vegetable crops (Keefer *et al.* 1986).

9.7 CONCLUSIONS

The most common word to describe sewage sludge nowadays is "Biosolids". Biosolids may be used as a resource in a number of sustainable ways instead of being considered and managed as a waste. Moreover biosolids may be used as a source of energy, reducing the dependence on fossil fuels, or for rehabilitation of contaminated land. These uses require consistency in the quality of biosolids, to a level depending on the intended use. This may be achieved only through proper management and effective controls. Also, biosolids application on land is the main practice and remains the most cost effective methods in the entire world. Biosolids physicochemical characteristics plays significant role before their final application. Moreover, a typical biosolids application program has the potential to supplement the soil nitrogen, phosphorous, organic nitrogen, organic matter and several nutrients. On the other hand there are some limitations for those nutrients as must not contain any heavy metals like As, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, and Zn. Furthermore, during biosolids application in soils (even though is a composted biosolids) must not exist the Country regulation regarding the maximum application rate. Sewage biosolids improves soil physical and chemical properties such as organic matter, water holding capacity, nutrients, pH balance, trace elements, stability and workability. In addition they enhance biological activity, through greater water retention and aeration stimulating root growth, increased worm and micro-organism populations.

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Chapter 10

Anaerobic digestion and energy recovery from wastewater sludge

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10.1 PRODUCTION AND CHARACTERISTICS OF WASTEWATER SLUDGE

The main aim of wastewater treatment is producing an effluent of good quality which can be released in the environment: the typical by-product of this process is sludge. Even though sludge differs for origins and characteristics, in general, sludge disposal is one of the main cost, together with energy and labour, for wastewater management. In a wastewater treatment facility it can be distinguished sludge produced in preliminary treatments, primary sludge, produced in primary settlers, biological sludge originated from microorganisms growth (typically in activated sludge processes), and chemical sludge produced in tertiary treatments (e.g., phosphorus post-precipitation or suspended solids removal). While primary and biological sludge are a carbon rich material and need to be processed and stabilised before they are disposed of, the others are basically inert or inorganic sludge.

The amount of produced stabilised sludge is of primary importance: it is around 10 million and 6 million tons dry matter in EU-27 (Eurostat, 2014) and US, respectively (Kelessidis & Stasinakis, 2012).

In this chapter we will mainly consider the treatment of primary and biological sludge through anaerobic digestion: in fact this bio-process allows for several benefits, like mass and volume reduction, biogas recovery, and hygienisation. Because of the different characteristics of these two types of sludge, the yields and effectiveness of the AD process can differ a lot.

10.1.1 Primary sludge

Primary sludge is produced in primary settlers through the sedimentation of suspended solids. Depending on the settling efficiency, approximately 40–60% of influent suspended solids (and COD) settle and is removed in this operation unit. The produced solids are in the range of 45–60 g total solids per Person Equivalent (PE) per day while the correspondent volume is 0.9–2.2 litres per PE per day. Total solids are therefore in the range of 1–6%. Nitrogen and phosphorus contents are in the range of 1–5% and 0.6–2.8%, respectively, on a dry matter basis. Solids removal in primary settler can be enhanced by co-settling with activated sludge or by adding flocculating chemicals: in these cases the amount of produced primary sludge is increased.

10.1.2 Secondary (biological) sludge

Biological (or secondary) sludge is the result of bacterial growth within the activated sludge process. In general some 50% of the destroyed influent BOD is converted into new biomass, thus "sludge" (Metcalf & Eddy, 2013).

With specific reference to data reported in Table 10.1, the produced solids are generally in the range of 25–45 g total solids per Person Equivalent (PE) per day while the correspondent volume is 1.4–7.3 litres per PE per day. Total solids concentrations are therefore low and typically in the range of 0.5–1.5%. Nitrogen and phosphorus contents are in the range of 2.5–6% and 1–6% on a dry matter basis. The highest value for P depends on the adopted process for P removal, chemical or biological, within the activate sludge process (Metcalf & Eddy, 2013).

The biodegradability and biogas recovery of biogas from biological sludge is also related to the process operation: for example, large solid retention times in the activated sludge process determine a partial stabilisation of sludge with consequent decrease of the available carbon content (Vogel *et al.* 2000). As a consequence, low biogas yields are observed for secondary sludge originated in WWTPs adopting large SRTs (Bolzonella *et al.* 2005).

Mix of primary and secondary sludge show different characteristics depending on the predominance of the one or the other. Table 10.1 resumes the main characteristics of mixed sludge.

Table 10.1 Characteristics and production of primary, biological and mixed sludge.

Sludge Type	Production, L per PE per day	Production, gTS per PE per day	Total Solids, %	TN, % TS	TP, % TS
Primary sludge	0.9–2.2	45–60	1–6	1–5	0.6–2.8
Waste activated sludge	1.4–7.3	25–45	0.5–1.5	2.5–6	1–6*
Mixed sludge	1.9–4.3	50–70	3–6	4–6	1–3

*If P co-precipitation or biological up-take are applied.

10.1.3 Treatment and disposal of sludge

Produced sludge within the wastewater treatment process is normally stabilised via aerobic or anaerobic biological, or rarely chemical, processes so to reduce its content in putrescible material. Stabilised sludge, depending on its quality, can be used for land application, or disposed of through landfilling or incineration. Despite the final disposal route (Mininni, 2015) a step for stabilisation and volume reduction is often present: in medium-large WWTPs anaerobic digestion is the preferred process to achieved this aim.

10.2 ANAEROBIC DIGESTION OF WASTEWATER SLUDGE

Anaerobic digestion of excess sludge is typically present in medium-large WWTPs: as a general rule anaerobic digesters, because of their considerable capital costs, are present in WWPTs larger than 30,000 PE (more than 7500 m^3 wastewater treated per day). Historically, AD was primarily used because of its capability of reducing pathogens and odour. Only in a second moment other important features like mass reduction and biogas production were considered.

The conventional anaerobic digestion single stage mesophilic process, the most popular adopted for sludge digestion in large WWTPs, is capable of converting the organic matter of sludge into biogas, reducing its mass. It operates at low rate: organic loading rate (OLR) is in the range of 0.5–1.5 kgVS per m^3 per day while retention time can be as high as 50–60 days. Because of the different characteristics of sludge (see Table 10.1), the bio-conversion of organic matter is variable. The methanogenic process is generally limited by the rate of the hydrolysis of organic matter. In general, primary sludge, because of the presence of cellulose and oil/grease, is relatively easier to be degraded while biological sludge, which is composed of aerobic bacteria capsuled in biopolymers, is difficult to degrade. The expected biogas production (on influent and destroyed VS) and VS percentage removal are reported in Table 10.2 (adapted from Bolzonella *et al.* 2002, 2005).

Table 10.2 Expected biogas production and VS removal.

Type of Sludge	SGP, m^3/kgVS Fed	SGP, m^3/kgVS Destroyed	VS Removal, %
Primary	0.3–0.5	0.8–1.1	40–50
Biological	0.2–0.3	0.6–0.8	20–30
Mixed (typical)	0.3–0.4	0.8–1.0	30–40

With specific reference to data reported in Table 10.1 and Table 10.2 the expected specific biogas productions are in the range of 10–20 litres per PE per day. This biogas can be used in heaters, for digesters warming, while when excess biogas is produced, also power can be generated via co-generation, turbines, or fuel cells. In these cases, the power self-generation can cover 30–40% of the energy requirements for wastewater treatment (fixed at 30 kWh per PE per year, Bodik & Kubaska, 2013). An alternative option can be the upgrade of produced biogas to biomethane for grid injection or the automotive refill.

Beside mesophilic environment also thermophilic processes can be applied (Zabranska *et al.* 2002; Bolzonella *et al.* 2012). Thermophilic AD offers several advantages over traditional mesophilic processes: increased rates of methane production, decreased fluid viscosity, decreased biomass formation increased formation of organic matter from waste to biogas and increased pathogen inactivation, which is an important aspect for the definition of class A biosolids in the US regulation (Iranpour *et al.* 2006). In general, enhancement of biogas yields and associated VS destruction, are in the range of 10–30% when adopting a thermophilic process. Clearly, if compared with a conventional mesophilic process, the application of a thermophilic process requires for adapt infrastructures (type of concrete and steel, heat exchangers) and skilled personnel. On the other hand, potential drawbacks like smell generation, worsened dewatering, and process instability due to high free ammonia concentrations should be taken into account (De la Rubia *et al.* 2013).

10.3 MULTI STAGE AND TEMPERATURE PHASED ANAEROBIC PROCESS

It is widely accepted that the initial hydrolysis of particulate organic matter to soluble substances is the rate-limiting step of anaerobic digestion of sludge, in particular in anaerobic digestion of waste activated sludge. The phase separation of hydrolysis/fermentation from methanogenesis in different reaction environments may lead to a larger biogas yield and optimize the overall reaction rate, with regard to stability and substrate degradation efficiencies in both reactors (Demirer & Othman, 2008). In fact, in such a configuration, different bacterial populations are provided with the best conditions to operate in the two reactors (Lv *et al.* 2010). The application of an hydrolysis step before methanisation in a two phase anaerobic digestion process relies as a biological pretreatment method of sludge, and in particular waste activated sludge, and has been widely applied at full scale especially in the US (Speece, 1988): in fact, it was demonstrated that the use of a multi-stage environment in the first stage processes improves the conversion capability of sludge into biogas in anaerobic digesters (Wilson *et al.* 2008) as well as the characteristics of the final biosolids (Iranpour *et al.* 2006).

A particular kind of multi stage process is the temperature phased process (TPAD): in this case there is an hydrolysis step before methanisation in a two-step anaerobic digestion process where the two stages generally operate at different temperatures (Cheunbarn & Pagilla, 2000; Ge *et al.* 2011). Extensive work on TPAD has been carried out in the US with the particular aim of achieving class A biosolids (e.g., Santha *et al.* 2006) while there is still a limited experience in Europe (Oles *et al.* 1997).

10.4 PRE-TREATMENT OF SLUDGE FOR ENHANCED ANAEROBIC DIGESTION

The AD process is generally limited by the rate of the hydrolysis of particulate organic matter. Efficient pre treatments brake down organic matter and cells and improve the surface available for enzymes attack.

In general, pre-treatments enhance the rate of the bioprocess rather than the potential biogas production. Pre-treatments are therefore more efficient for systems with limited volumes and retention times. The key of this alternative is the optimization of the anaerobic digestion process (biodegradability and degradation rate enhancement, digesters load increase, sludge reduction) together with the achievement of some other benefits (sanitization, dewatering enhancement, removal of emerging micropollutants). A number of pre-treatment alternatives (thermal, chemical, mechanical, electrical, ultrasound) have been tested and an extended literature is available (Carrere *et al.* 2010), however, up to date, only thermal/high pressure processes is effectively applied at full scale. In fact, technical and especially economic constraints of most of the tested technologies have limited their scale-up to field implementation. This is the reason why pre-treatments are applied only in very specific situations like in the case of limited digester volumes or very high disposal costs. In all other situations the return of investment for pre-treatments is never reached (Boehler & Siegrist, 2006).

A thermal/high pressure pre-treatment consists of subjecting the sludge to high temperature and high pressure in an hydrolysis reactor. Several commercial technologies have been developed that follow this common principle, but with different operation schemes. Seven different thermal hydrolysis technologies are commercially available in 2016 for the treatment of municipal sewage sludge: Cambi (THP), Veolia (Exelys), SH + E(Lysotherm), Sustec (TurboTec), Haarslev (ACH), Aqualogy (Aqualysis), teCH4+ (tH4+) (Ponsa *et al.* 2017). Generally, in all processes, the temperature applied is around 165–170°C for 15–30 minutes while steam explosion can be used or not. Only in one case (teCH4+) temperatures > 220°C are applied.

The use of a pre-treatment step can increase the biogas yield up to 40–50% keeping the HRT constant, but also influences other different important aspects: mass reduction (proportional to biogas generated), lower viscosity (better pumping and mixing) possibility to operate at higher total solids and organic loading rates and, sometimes, improved dewaterability.

Important issues to consider for thermal/high pressure applications are: capital and managing costs, system complexity, need for skilled operators, and increase in soluble inert fraction and ammonia in the recycled stream.

10.5 ANAEROBIC DIGESTION OF SLUDGE AND OTHER SUBSTRATES (CO-DIGESTION)

In most cases fractions of digester volumes are available, especially when only WAS is treated. In these cases, substrates other than sludge can be anaerobically co-digested to increase the energy recovery. In fact, an interesting option for improving methane yields in WWTPs is Anaerobic co-Digestion (AcoD) of sludge and other organic waste like the organic fraction of municipal solid waste (OFMSW), food waste (FW), fat oil and grease (FOG), agro-waste and others (Mata-Alvarez *et al.* 2014).

Clearly it is important to choose the best co-substrate and blending ratio with the aim of favouring synergisms, diluting harmful compounds, optimizing methane production while preserving the digestate quality.

Historically, AcoD of sludge with the organic fraction of municipal solid waste (OFMSW) or food (FW) or kitchen waste (KW), three substrates with similar characteristics, are the most reported co-digestion examples but a number of different options can be found in actual practice (Bolzonella *et al.* 2006; Koch *et al.* 2015). When looking at the US scenario however the co-digestion of fats, oils and greases (FOG) is also reported (Long *et al.* 2012).

The low organic load determined by sludge (often < 1 kgVS/m^3 per day) together with the un-used capacity of many wastewater treatment plants (WWTP) is the main driving force behind SS co-digestion. SS is characterized by relatively low C/N ratio and high buffer capacity. Therefore, it is able to stand co-substrates with high amounts of easily biodegradable organic matter and with low alkalinity values. The main aim of the approach is to improve biogas production and energy recovery up to levels similar to those of the energy demand of the WWTP (Bodik & Kubaska, 2013). While doing so, the WWTP becomes a local centre for waste disposal. Clearly, the good quality of final digestate and its potential reuse remains a prerequisite.

There are now a considerable number of WWTPs applying the co-digestion option around Europe and worldwide. Depending on the quality of the treated co-substrate and available free volume in the digester, biogas increase can range from 10 to 50% after co-digestion implementation with considerable improvements in the energy balance of the WWTP: in general, the typical energy required for wastewater treatment is in the range of 20–30 kWh per person equivalent per year, while digestion of mixed sludge can produce up to 10–15 kWh per person equivalent per year in the best conditions, co-digestion can help to cover this demand up to energy independency.

Specific constrains to the application of the AcoD regime are related to the pre-treatment step (preparation of the feeding material), to reactor configuration (mixing, heat exchangers) and to the pollutant loadings recycling to the wastewater treatment line determined by the reject water. Also the presence of inert material, like plastics or glass, in the produced biosolids are important aspects.

10.6 NOVEL SHORT-CUT TREATMENT OF SLUDGE REJECT WATER FOR NUTRIENT AND CARBON MANAGEMENT

Sludge reject water is a nutrient-rich flux which should be properly managed to optimise the nitrogen removal and phosphorus recovery in wastewater treatment plants (WWTPs). Completely autotrophic nitrogen removal is the most attractive biological process for the treatment of sludge reject waters in municipal WWTPs with fast growing number of full-scale applications (Lackner *et al.* 2014). However, this process cannot enhance the phosphorus bioaccumulation and should be followed by struvite crystallisation for sustainable phosphorus recovery. Recently, a novel scheme was developed for nitrifying and denitrifying ammonium via-nitrite while accomplishing biological phosphorus removal. This process was applied to treat: (1) sludge reject water (Fatone *et al.* 2016); (2) supernatant after anaerobic co-digestion of sewage sludge and OFMSW (Frison *et al.* 2013, 2016). This system, called with the acronym SCENA (Short-Cut Enhanced Nutrients Abatement), can be described according to the following key processes: (1) alkaline fermentation of sewage sludge (Longo *et al.* 2015) and/or OFMSW for the production of the best available carbon source (BACS) which is a VFA-mixture with the high content of propionic acid; (2) nitritation in aerobic conditions (DO > 1.5 mg/L, so as to also minimize N_2O emissions); (3) denitritation and via-nitrite biological phosphorus uptake achieved through the dosage of the BACS; (4) process control on the basis of low-cost sensors of pH, conductivity and redox potential. The SCENA system has been applied to revamp the Carbonera WWTP (Italy) managed by the water utility Alto Trevigiano Servizi srl. During the first year of operation, the SCENA operation and maintenance (O&M) costs of 1.6 €/kg$N_{removed}$ are much lower than the O&M cost of the mainline (3.5 €/kg$N_{removed}$, Fatone *et al.* 2016) even not taking into account the technical and economic advantages in terms of via-nitrite enhanced phosphorus uptake. Currently optimization of the BACS production and process control is under investigation and the SCENA system will be fully industrialized within the Horizon 2020 Innovation Action "SMART-Plant" (www.smart-plant.eu), so as to be widely replicable in municipal WWTPs. Most recently the short-cut nitrogen removal has been coupled to the recovery of polyhydroxyalkanoates (PHA) in the novel SCEPPHAR (Short-Cut Phosphorus and PHA Recovery) system. In this novel scheme the biological nitrogen removal via nitrite was integrated with the selection of PHA storing biomass in the sludge treatment line. The integration of PHA production within a WWTP at full scale was the driving force for the development of this novel treatment scheme. A 2-fold objective was achieved: enhanced selection of PHA stored biomass and reject water treatment for nitrogen removal. Thus, the examined process provides true added value toward the effective treatment of nitrogen in highly contaminated effluents within WWTPs, aiming at the same time to maximize resource recovery through polymer production, which could enhance the sustainability of the WWTP (Frison *et al.* 2015). The scale-up of the SCEPPHAR system will be carried out within the Horizon 2020 SMART-Plant Innovation Action within the Carbonera WWTPs, in parallel to the SCENA system.

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Chapter 11

Advanced oxidation processes for wastewater treatment

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11.1 INTRODUCTION

Advanced oxidation processes (AOPs) or technologies (AOTs) constitute a family of similar but not identical processes that rely on the intermediacy of reactive oxygen species (ROS) to induce redox reactions in waters, wastewaters, soils, sludges and in the gas phase. The family comprises processes such as semiconductor photocatalysis, photo-Fenton and alike reactions, dark Fenton and alike reactions, ozonation, electrochemical oxidation, sonochemical oxidation, non-thermal plasma, γ-rays and thermochemical processes such as wet air oxidation (WAO). Moreover, various combinations of the above processes have been tested in the quest of more efficient environmental technologies.

Over the past 30 years, R&D on the environmental applications of AOPs has blossomed with emphasis given on water/wastewater treatment for the removal of organic contaminants, inorganics and pathogens. This is primarily but not exclusively achieved by the oxidative action of hydroxyl radical ($^{\bullet}OH$), a short-lived, non-selective ROS with a redox potential of ca 2.8 V, i.e. second only to fluorine. In fact, the hydroxyl radical is the binding link amongst the various AOPs although other oxidants may be equally (or even more) important depending on the process and the operating conditions in question. For example, photogenerated valence band holes, molecular ozone, electrogenerated hydrogen peroxide, chlorine and chlorohydroxyl radicals, and WAO-produced organic radicals are such oxidants, just to name a few.

The need to develop AOPs in water treatment is closely related to the inadequacy of biological processes to treat persistent and emerging contaminants in aqueous matrices including e.g. (i) residual pesticides in surface and ground waters,

(ii) pharmaceuticals and personal care products (PPCPs) and their metabolites in secondary treated effluents, (iii) heavily polluted industrial effluents. Moreover, AOPs are being employed for water disinfection; this is because many by-products of chlorination, the most commonly employed disinfection technique, have already been documented as toxic and carcinogenic (Pablos *et al.* 2013), while certain pathogens, like bacterial spores, protozoan cysts and viruses, exhibit considerable tolerance to chlorine, which imposes their more stringent control (Dunlop *et al.* 2008).

This chapter will discuss the advantages and drawbacks of AOPs for wastewater treatment through a number of case studies. The authors' intention is not to describe all possible AOPs and their water treatment applications as this would practically be impossible in the context of a book chapter. However, IWA has published a comprehensive book on AOPs (Parsons, 2004), where the reader can find detailed information on the fundamentals and applications of each AOP.

11.2 THE ROLE OF THE WATER MATRIX

The majority of published research on AOPs for water remediation is being performed in model aqueous solutions containing the contaminant under consideration. Most commonly, the contaminant is spiked in ultrapure water (UPW) at concentrations that typically are several orders of magnitude greater than those found in actual environmental samples and its degradation is monitored during some kind of AOP operating batch-wise. This approach has certain advantages since (i) it eliminates the interactions amongst the contaminant, the oxidative species and the constituents of more complex matrices (i.e. surface water, groundwater, municipal wastewater), (ii) it does not require sophisticated and laborious analytical techniques to monitor trace amounts of the contaminant, and (iii) data collection in batch or semi-batch systems is less time-consuming than in flow-through (i.e. continuous) systems.

Of the above, the quality of the actual water matrix is critical since not taking into account the various interactions is likely to lead to false conclusions. As a rule of thumb, degradation kinetics decrease with increasing matrix complexity and a typical example is shown in Figure 11.1, where the antibiotic sulfamethoxazole is subject to photocatalytic degradation using iron-doped TiO_2 as the photocatalyst, simulated solar light and four matrices, namely: UPW, drinking water (DW), secondary treated municipal wastewater (WW) and UPW spiked with 10 mg/L humic acid (HA used as a representative of the natural organic matter typically found in natural waters). The degradation rate, in this case, decreases in the order UPW > DW > WW ~ UPW + HA and verifies the aforementioned rule. Drinking water contains mainly anions and some cations, of which bicarbonates are the dominant ones in terms of concentration (in the order of 200–300 mg/L). Bicarbonates are known to react with hydroxyl radicals forming eventually carbonate radicals that are weaker oxidants (by about 25%) and this would explain the reduced degradation rates in DW (Tercero Espinoza *et al.* 2007):

$$HCO_3^- + \bullet OH \rightarrow \bullet CO_3^- + H_2O \tag{11.1}$$

$$\bullet CO_3^- + \bullet CO_3^- \rightarrow CO_2 + CO_4^{2-} \tag{11.2}$$

Other anions such as nitrates, chlorides and sulfates can also act as scavengers of hydroxyl radicals, thus contributing to lower kinetics.

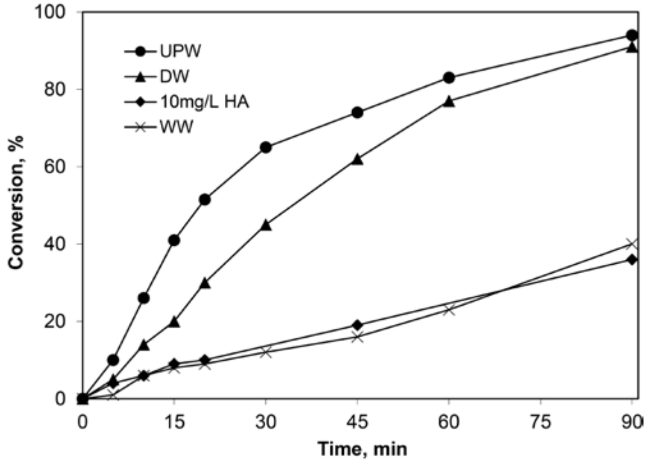

Figure 11.1 The effect of water matrix on sulfamethoxazole (235 μg/L) degradation during simulated solar light at 7.3 10^{-7} einstein/(L.s) with 1 g/L of 0.04%Fe/TiO_2 photocatalyst. Other conditions: Liquid volume of 120 mL and inherent pH of 6.2 for UPW, 7 for DW and 8 for WW.

Secondary treated wastewater contains a few mg/L of the so-called effluent organic matter (EfOM), which competes with the target contaminant for ROS; since the latter are generally non-selective, they are wasted to unwanted reactions with the quite stable EfOM (Antonopoulou *et al.* 2015). Another rule that usually occurs is that the adverse impact of non-target organics (like HA or EfOM in Figure 11.1) on kinetics is more important than that of non-target inorganics (like DW in Figure 11.1). Although it looks irrelevant at a first glance, it is a strong indication that working with contaminant concentrations that are well outside the environmentally relevant ones will flaw reaction kinetics. Keeping things as simple as possible, a power-law rate expression can be employed to simulate kinetics:

$$-\frac{dC}{dt} = k_{\text{app}} C^n \tag{11.3}$$

where C is the contaminant concentration, k_{app} is an apparent rate constant and n is the order of the reaction. For semi-batch systems, where ROS are produced at a fixed rate (this would include photochemical, sonochemical, electrochemical, microwave AOPs), k_{app} embodies the (nearly) constant concentration of ROS (this is a fair assumption), while the reaction order takes values of zero or one or anything between zero and one. This is because kinetics are determined by the ratio of ROS to contaminant concentration; at a simple level, if ROS are in excess then the reaction approaches first order, while zeroth order is expected at high contaminant concentrations.

Going back to the water matrix effect, each rule has its own exceptions that are case-specific, i.e. they depend on the type of AOP and the contaminants in question. Some examples are as follows:

1) The carbonate radical is a strong one-electron oxidant exhibiting selective reactivity towards aromatic compounds. Moreover, the rate of carbonate radical recombination according to reaction (11.2) is two orders of magnitude slower than the respective rate of hydroxyl radicals, thus giving the carbonate radicals the chance to diffuse and react with the target compound (Augusto *et al.* 2002; Petrier *et al.* 2010; Zhang *et al.* 2015). Therefore and depending on the conditions in question, the detrimental effect of hydroxyl radical scavenging by bicarbonates may be counterbalanced by the oxidative action of carbonate radicals.
2) Electrochemical processes occurring in a matrix containing chlorides generate primary and secondary oxidants such as free chlorine, HClO and/or ClO^-, and ClO_2^- (Rajkumar *et al.* 2007; Sires & Brillas, 2012). These species are very active oxidants and their presence usually offsets the partial loss of hydroxyl radicals that are scavenged by chlorides to form chlorine radicals (see also Section 11.3.3.2).
3) In photochemical/photocatalytic processes, the presence of humic acid may accelerate kinetics through various mechanisms including (i) sensitization of the photocatalyst, (ii) trapping of conduction band electrons, and (ii) generation of extra ROS from HA photolysis (Cho & Choi, 2002; Vinodgopal & Kamat, 1992; Xu *et al.* 2011).

11.3 ENHANCEMENT OF PROCESS PERFORMANCE

It is generally accepted that degradation rates by AOPs can adversely be affected by several factors including, besides the complexity of the water matrix, the type and concentration of the contaminant, the type and concentration of the oxidants and catalysts, and the reactor configuration. In this perspective, several strategies have been researched to improve degradation kinetics, as follows.

11.3.1 Coupling of AOPs

The simultaneous application of two or more AOPs is a step to the right direction increasing the oxidative capacity of the combined process due to (i) the increased production of ROS (i.e. cumulative effect), and/or (ii) positive interactions amongst the individual processes (i.e. synergistic effect).

This is demonstrated in Figure 11.2, which shows the degradation of propyl paraben (a moderate endocrine disruptor) by means of sulfate-radical oxidation. Sodium persulfate (SPS) has recently attracted the attention of the scientific community as a promising source of sulfate radicals because of its moderate cost, high stability and aqueous solubility, as well as the fact that it is solid at ambient temperature, which facilitates its transport and storage (Lin *et al.* 2011). Persulfate activation to produce sulfate radicals can be achieved by a number of methods including high temperatures, the presence of transition metals (mainly iron), ultraviolet irradiation, microwaves and ultrasound (US) irradiation. When SPS is activated by 20 kHz ultrasound, 90% paraben conversion is achieved in 60 min; half this time is needed for the same conversion when SPS is activated by an iron-containing magnetic carbon xerogel. Notably, when the two activators are used together, the time needed for 90% conversion is just 4 min. If this were the result of a purely additive effect, the conversion-time profile of the combined process would be represented by the dashed line; evidently, the interaction is synergistic since the rate of the combined process is greater than the sum of the rates of the individual processes. This may be attributed to the ultrasound (i) facilitating mixing of the reactor contents, thus minimizing mass transfer limitations, and/or (ii) altering the surface properties of the heterogeneous catalyst.

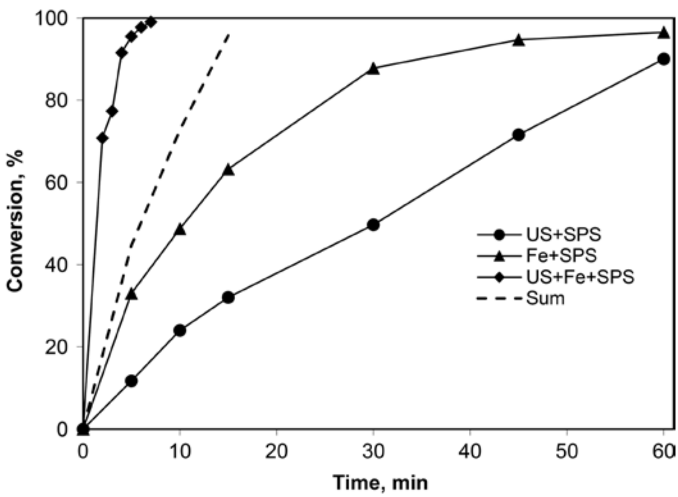

Figure 11.2 Degradation of propyl paraben (420 µg/L) in UPW using 500 mg/L of SPS and either 50 mg/L of an iron-containing magnetic carbon xerogel or ultrasound at 36 W/L power density, pH 3, 25°C and 120 mL of liquid volume. The graph shows the effect of process coupling relative to the individual processes.

In general, the synergy (S) can be quantified as the normalized difference between the rate constants obtained under the combined process (k_{combined}) and the sum of those obtained under the separate processes (k_i):

$$S = \frac{k_{\text{combined}} - \sum_{1}^{n} k_i}{k_{\text{combined}}} \tag{11.4}$$

$$\text{where} \quad S\begin{cases} >0 & \text{synergistic effect} \\ =0 & \text{cumulative effect} \\ <0 & \text{antagonistic effect} \end{cases} \tag{11.5}$$

Although not very common, AOPs coupling may result in inhibitory (antagonistic) effects, thus leading to decreased degradation rates. A possible reason is the generation of large amounts of ROS that may behave as self-scavengers.

The adverse effect of radicals in excess is demonstrated in Figure 11.3, which shows the extent of bisphenol A (another endocrine disruptor) as a function of SPS concentration; in this case, SPS is activated by a bimetallic carbon xerogel containing iron and cobalt. Degradation increases as SPS concentration increases from 62 to 250 mg/L, while a further concentration increase to 500 mg/L results in reduced rates.

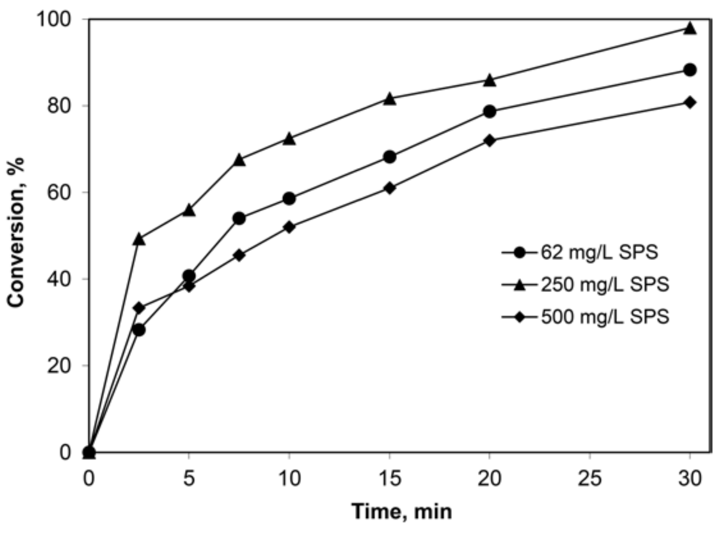

Figure 11.3 The effect of SPS concentration on bisphenol A (285 μg/L) degradation in UPW. The process is activated by a bimetallic Fe-Co-containing carbon xerogel (75 mg/L) at pH 3 and 120 mL of liquid volume.

11.3.2 How can selectivity be improved?

Bearing in mind that (i) AOPs are, in general, non-selective processes since the hydroxyl radical (i.e. the dominant oxidizing species) is non-selective itself, and (ii) most wastewaters, and in particular those originating from industrial processes, may contain a wide array of substances with varying physicochemical, biological and ecotoxic properties, a smart strategy is to increase process selectivity against the "nastier" chemicals of the effluent. Some examples how this strategy can be implemented are as follows:

1) Ozone oxidation at acidic and/or near-neutral conditions mainly occurs through direct reactions of molecular ozone with organic substrates in a process commonly known as ozonolysis. Ozone preferentially attacks double bonds and can be applied to destroy the chromophores (i.e. $N = N$ bonds) of dyes typically found in textile effluents, leading to complete decolorization. Moreover, effluents of agro-industrial origin (e.g. olive oil and table olives production, wine-making) contain polyphenolic compounds that are responsible for low biodegradability and can selectively be removed by ozonolysis (Karageorgos *et al.* 2006).
2) Integrating AOPs and biological processes has traditionally been employed for the treatment of effluents containing bioresistant and biodegradable fractions (Comninellis *et al.* 2008). Typically, a biological pre-treatment step is applied to remove the biodegradable fraction followed by AOPs post-treatment as a final, polishing step. This is expected to reduce treatment costs considering that bioprocesses are less costly and more environmentally friendly than other treatment technologies. The concept of process integration does not exclude other scenarios, i.e. AOPs → biological treatment or biological treatment → AOPs → biological treatment depending on the effluent under consideration and the treatment objectives.
3) Integrating AOPs with separation processes may also prove beneficial for specific types of effluents containing e.g. lots of solids (e.g. agro-industrial effluents), volatile organics (e.g. effluents from electronic processing) and macromolecules. Solids must be removed first by filtration, sedimentation or coagulation, otherwise they can be dissolved during advanced oxidation and consequently increase the organic loading of the liquid phase. Moreover and in the case of photochemical AOPs, the increased effluent opacity may be detrimental to the process. In the case of polymer-processing effluents containing macromolecules of varying molecular size, an attractive option includes the application of ultrafiltration in between AOPs and biological post-treatment; chemical oxidation can easily break down large macromolecules to more biogenic oligomers and ultrafiltration can guarantee that only molecules of certain size, below the membrane's cut-off, are fed to the biological reactor.

4) No matter how complex the original effluent is, the fast propagation of radical-induced and other reactions will generate numerous transformation by-products through various reaction pathways. Although it is practically impossible to identify the full set of by-products even with the most sophisticated analytical techniques, the distribution of key compounds in the reaction mixture can be determined, alongside gross parameters such as biodegradability and toxicity indices. The use of suitable catalysts such as transition metal oxides and noble metals in e.g. WAO processes may alter the relative distribution of by-products compared to the respective uncatalyzed process and favor the formation of more biodegradable and/or less toxic compounds. Moreover, catalysts will accelerate partial oxidation reactions, thus leading to effluent's mineralization (Quintanilla *et al.* 2006).

11.3.3 New or improved materials

11.3.3.1 Heterogeneous semiconductor photocatalysis

Semiconductor photocatalysis based on titanium dioxide is, perhaps, the most widely investigated AOP for the destruction and mineralization of a wide range of organic contaminants and microorganisms (Carp *et al.* 2004). TiO_2 photocatalyst exhibits several advantages including low cost, availability at various crystalline forms and particle characteristics, lack of toxicity and photochemical stability. A major shortcoming has to do with its wide band gap energy of about 3 eV, which means that only ultraviolet radiation can be used for its photoactivation. This limits the use of zero-cost natural sunlight since solar radiation reaching the surface of the earth contains only about 3–5% UV radiation. In this respect, it is of great interest to find ways to extend the absorbance wavelength range of TiO_2 to the visible region without the decrease of photocatalytic activity. During the last years, studies have focused on the improvement of TiO_2 photocatalytic efficiency by several methods such as generating defect structures, doping with metallic or non-metallic elements or modifying the TiO_2 surface with noble metals or other semiconductors (Pelaez *et al.* 2012).

Another strategy is the development of new materials that can predominantly be activated in the visible region; silver orthophosphate (Ag_3PO_4) is a low band-gap photocatalyst that has attracted enormous attention in the past few years due to its great potential in harvesting solar energy for environmental purification and oxygen evolution. More importantly, this novel photocatalyst can achieve a quantum efficiency of up to 90% at wavelengths >420 nm, thus implying a very low electron-hole recombination rate (Yi *et al.* 2010). A drawback of silver orthophosphate is its insufficient long-term stability since it is photochemically decomposed in the absence of a sacrificial agent. This can be overcome covering the surface of Ag_3PO_4 with metallic silver nanoparticles which create localized surface plasmon resonance effects and/or synthesizing various Ag_3PO_4-based composites. The superiority of Ag_3PO_4 over TiO_2 is demonstrated in Figure 11.4, which compares the photocatalytic degradation of antibiotic sulfamethoxazole under simulated solar irradiation with the aforementioned catalysts; it is evident that P25 TiO_2, a benchmark photocatalyst for numerous environmental applications, is far less active than Ag_3PO_4.

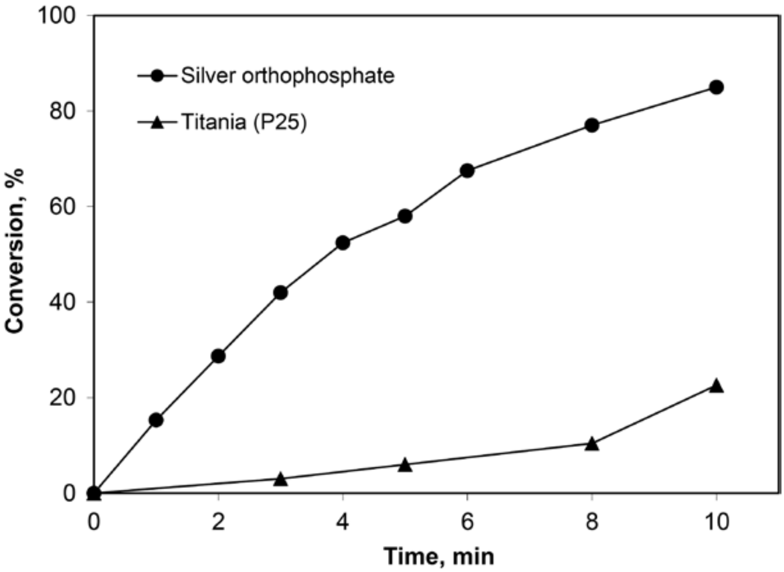

Figure 11.4 Photocatalytic degradation of sulfamethoxazole (525 μg/L) in UPW under simulated solar light (7.3 10^{-7} einstein/(L.s)) and 50 mg/L of photocatalyst, pH 6 and liquid volume of 120 mL.

11.3.3.2 Anodic oxidation

In recent years, electrochemical oxidation has attracted considerable attention as a water remediation technology (Sarkka *et al.* 2015). The process is environmentally friendly in the sense that it does not require additional chemicals or oxidants, while the major cost element is associated with energy consumption; this could be minimized using photovoltaics to power the system, thus leading to a low-cost green technology.

The type of anodic material is critical in determining process efficiency; in this context, various types of anodes have been tested such as stainless steel, graphite, Pt, TiO_2, IrO_2, PbO_2 and several Ti-based alloys (Sires & Brillas, 2012). Boron-doped diamond (BDD) has recently emerged as a very promising anodic material for environmental applications since it can promote the degradation and mineralization of organic compounds. Using this anode at high potential, highly reactive hydroxyl radicals are generated on its surface:

$$BDD + H_2O \rightarrow BDD(HO^{\bullet}) + H^+ + e^- \tag{11.6}$$

The radicals are weakly adsorbed on the surface and can readily react with organic matter, R, leading to its mineralization (Sarkka *et al.* 2015; Sires & Brillas, 2012):

$$R + BDD(HO^{\bullet}) \rightarrow CO_2 + H_2O \tag{11.7}$$

The superiority of BDD anode over platinum and stainless steel is demonstrated in Figure 11.5, which shows the degradation of butyl paraben at 50 mA/cm^2 applied current density with sodium sulfate as the supporting electrolyte. Degradation rates with BDD are 4–7 times greater than with the other two anodes. Interestingly, when the reaction mixture is supplemented with 50 mg/L sodium chloride, the degradation is improved further (dashed line in Figure 11.5) and this is related to the contribution of indirect oxidation induced by Cl-containing oxidants; the latter are formed electrochemically from chloride ions that either exist inherently in the matrix (i.e. drinking water, municipal wastewater, certain industrial effluents) or they are added externally. Although the beneficial role of secondary oxidation on the rates is evident, the likely formation of hazardous organo-chlorinated by-products is a matter of serious concern (Radjenovic & Sedlak, 2015).

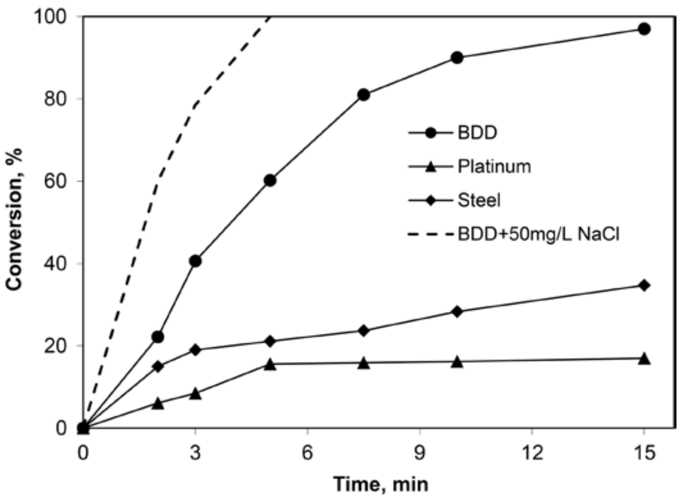

Figure 11.5 Effect of anodic material on the electrochemical oxidation of butyl paraben (490 μg/L) in UPW at 50 mA/cm^2 current density, 120 mL of liquid volume, pH = 6–6.5 and 0.1 M Na_2SO_4 as the supporting electrolyte.

11.4 PERSPECTIVES AND RECOMMENDATIONS

After so many years of research on AOPs for wastewater treatment, the proof of concept is already available; what is really missing though is the next step from the purely academic (lab- or pilot-scale) research to large-scale, fully operational applications. It is the authors' strong belief that the major obstacle is the level of specific cost (i.e. monies per unit mass of contaminant removed or unit volume of effluent treated) associated with AOPs and in comparison with other more "conventional" treatment techniques. How can AOPs become more attractive cost-wise? Some thoughts are as follows:

1) AOPs should not do and cannot do the "full monty". AOPs must be forced to become selective in the sense that they must have a well-defined treatment target, e.g. to remove micro-contaminants, to kill pathogens, to polish already treated industrial streams. Otherwise, precious and costly elements (oxidants, catalysts, energy) are wasted unnecessarily. In simple terms, battery treatment schemes must be considered, where AOPs need not have the first violin role.
2) The use of renewable energy sources is critical; in this sense, photochemical AOPs driven by sunlight have an obvious head start.
3) The field of AOPs can greatly benefit from advances in the area of materials science, where new materials with exciting properties are discovered. For instance, graphene materials have recently been tested with success as activators in sulfate-radical AOPs; this pinpoints the fact that AOPs for environmental applications is a topic lying at the interface of science and engineering and different disciplines must join forces to tackle the problem in a successful way.
4) Waste valorization is a relatively new and rather unexploited concept that could reduce treatment costs. The example of red mud, a residue from bauxite processing, containing iron oxides, titania and alumina is characteristic as this material can potentially serve as an AOP catalyst.
5) Public awareness must be enhanced and perceptions must be changed to digest that there is no such thing like "zero-cost" technology. Therefore, the best one can opt for is "low-tech, low-cost" technologies.

Overall, the complete replacement of existing treatment technologies by AOPs does not look promising from an economic point of view; this said, combination of AOPs with conventional wastewater treatment systems is conceptually feasible; this can happen in a sustainable manner if proper design, process optimization and smart thinking are applied.

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Chapter 12

Existence of organic micropollutants in the environment due to wastewater reuse and biosolids application

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12.1 INTRODUCTION

Organic micropollutants are compounds which are normally found at concentrations up to microgram per liter and milligram per kilogram in the aquatic and terrestrial environment, respectively, and they are considered to be potential threats to environmental ecosystems. Different groups of compounds are included in this category such as pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), perfluorinated compounds (PFCs), pharmaceuticals, surfactants, personal care products, estrogens and artificial sweeteners. Some of these compounds (e.g. organochlorine pesticides, PCBs, PAHs) have been studied in detail since 1980s, they are already included in the available national or international legislative documents and they are called *priority* substances. Others are characterized as *emerging* contaminants and no regulations currently require their environmental monitoring. The list of emerging contaminants is constantly expanding, as the development of advanced analytical methods allow the detection of new compounds in environmental samples (Subedi *et al*. 2014).

12.2 OCCURRENCE OF ORGANIC MICROPOLLUTANTS IN TREATED WASTEWATER AND BIOSOLIDS

Sewage Treatment Plants (STPs) are considered major point sources of organic micropollutants into the environment as they receive domestic and industrial wastewater as well as urban and -in some cases- agricultural runoff (Ratola *et al*. 2012; Luo *et al*. 2014; Arvaniti & Stasinakis, 2015). In a study conducted in STP of Athens (Greece) (Stasinakis *et al*. 2013), it was observed that among 36 emerging organic micropollutants belonging to different classes (synthetic endocrine disrupting compounds, pharmaceuticals, PFCs, benzotriazoles, and benzothiazoles), almost 30% of them was removed sufficiently during primary and secondary (activated sludge process with biological N, P removal; SRT: 9 d) wastewater treatment (>70% removal of efficiency), 30% was partially removed (30–69%), while the other compounds were not removed at all or even increased during treatment (Figure 12.1).

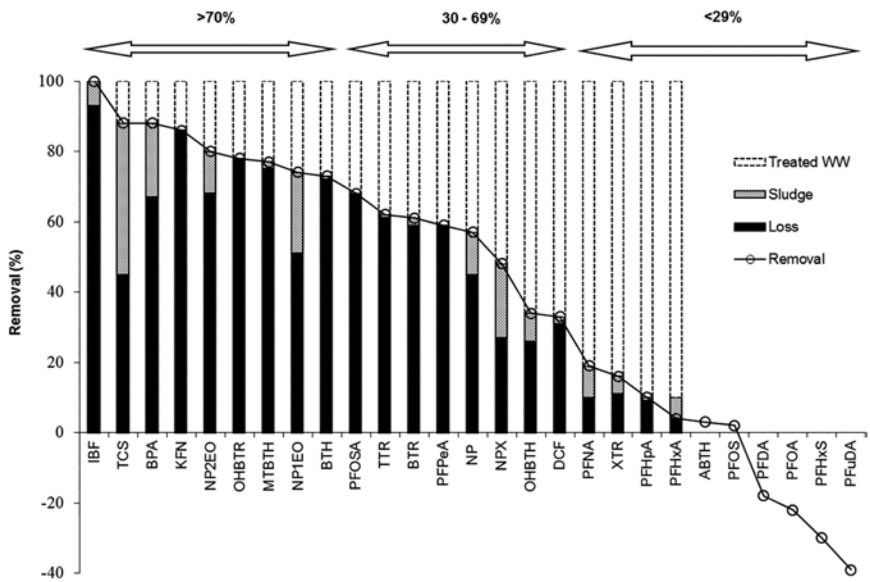

Figure 12.1 Removal efficiency (%) of the organic micropollutants during wastewater treatment and study of their fate in Athens STP The names of target micropollutants are given below: IBF: ibuprofen; TCS: triclosan; BPA: bisphenol A; KFN: ketoprofen; NP2EO: nonylphenol diethoxylate; OHBTR: hydroxybenzotriazole; MTBTH: 2-(methylthio)benzothiazole; NP1EO: nonylphenol monoethoxylate; BTH: benzothiazole; PFOSA: perfluorooctane sulfonamide; TTR: tolyltriazole; BTR: benzotriazole; PFPeA: perfluoropentanoic acid; NP: nonylphenol; NPX: naproxen; OHBTH: 2-hydroxybenzothiazole; DCF: diclofenac; PFNA: perfluorononanoic acid; XTR: xylytriazole; PFHpA: perfluoroheptanoic acid; PFHxA: perfluorohexanoic acid; ABTH: 2-aminobenzothiazole; PFOS: Perfluorooctanesulfonate; PFDA: perfluorodecanoic acid; PFOA: perfluorooctanoic acid; PFHxS: perfluorohexanesulfonate; PFuDA: perfluoroundecanoic acid). (*Reprinted from The Science of the Total Environment, 463–464, Stasinakis et al., Contribution of primary and secondary treatment on the removal of benzothiazoles, benzotriazoles, endocrine disruptors, pharmaceuticals and perfluorinated compounds in a sewage treatment plant, 1067–1075, 2013 with permission from Elsevier.*)

The main mechanisms affecting the fate of organic micropollutants during conventional wastewater treatment is (a) sorption to suspended solids and accumulation to the primary and secondary sludge and (b) biotransformation processes occurring in biological reactors (Verlicchi *et al.* 2012; Samaras *et al.* 2013; Stasinakis *et al.* 2013; Luo *et al.* 2014; Mazioti *et al.* 2015). Mechanisms such as volatilization, hydrolysis and photodegradation may also affect to a lesser extent the fate of organic micropollutants in STPs. Due to the partial removal of these compounds during wastewater treatment and the important role of sorption to sludge, significant concentrations of them are commonly detected in treated wastewater and sludge, worldwide.

Regarding treated wastewater, compounds such as phthalates, nonylphenols and artificial sweeteners have been detected at concentrations up to some tens μg L^{-1}, siloxanes and benzotriazoles usually range up to few μg L^{-1}, while concentrations of pesticides and most pharmaceuticals rarely exceed 1000 ng L^{-1} (Figure 12.2) (Bletsou *et al.* 2013; Samaras *et al.* 2013; Luo *et al.* 2014; Zolfaghari *et al.* 2014; Arvaniti & Stasinakis, 2015; Petrie *et al.* 2015; Gatidou *et al.* 2016). Having in mind the great number of micropollutants found in wastewater and the (bio)transformation processes occurring during wastewater treatment, a plethora of transformation by-products is also expected in treated wastewater. Their identification is an important issue due to their unknown toxicity and fate to the environment (Petrie *et al.* 2015). During the last years, the use of high resolution mass spectrometry screening methods have resulted to the publication of some relevant articles (Schymanski *et al.* 2014; Bletsou *et al.* 2015), however much more information is needed on the field.

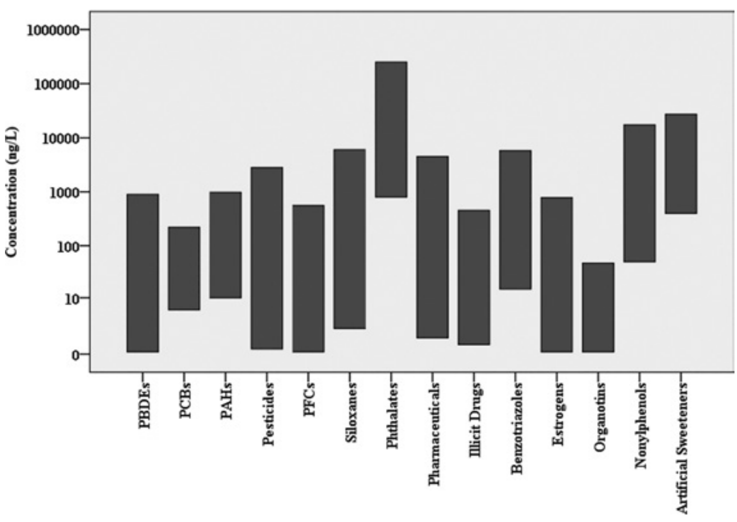

Figure 12.2 Reported ranges of organic micropollutants' concentrations in treated wastewater samples.

The concentrations of organic micropollutants in biosolids are frequently correlated with their concentrations in raw wastewater (Fent, 1996; Stasinakis *et al.* 2008). They are also affected by their physicochemical properties (hydrophobicity, molecular weight, water solubility, pKa) (Janex-Habibi *et al.* 2009; Clara *et al.* 2010), the characteristics of sludge (organic matter, pH, concentrations of cations) and the type of treatment provided in each STP (existence or not of primary sedimentation, retention times in different tanks, sludge stabilization method) (Heidler & Halden, 2009; Janex-Habibi *et al.* 2009; Stasinakis, 2012). Among the compounds that have been detected at the highest concentrations in biosolids are PAHs, nonylphenols and phthalates reaching up to some hundreds mg Kg^{-1} (Figure 12.3), while lower concentrations are usually found for pharmaceuticals, PCBs, PFCs and other organic micropollutants (Katsoyiannis & Samara, 2004; McClellan & Halden, 2010; Tancal *et al.* 2011; Clarke & Smith, 2011; Stasinakis, 2012; Mailler *et al.* 2014; Subedi *et al.* 2014; Venkatesan & Halden, 2014).

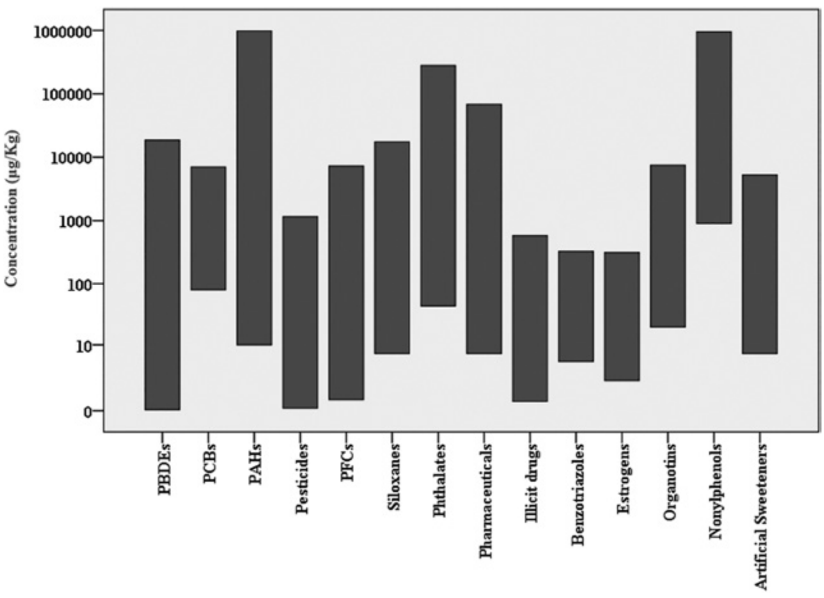

Figure 12.3 Reported ranges of organic micropollutants' concentrations in sludge samples (as µg Kg^{-1} d.w.).

12.3 FATE OF ORGANIC MICROPOLLUTANTS DURING WASTEWATER REUSE AND BIOSOLIDS APPLICATION

Treated wastewater reuse is a common practice in countries facing water shortage problems, while the urban reuse of wastewater gains ground worldwide (Fatta *et al.*

2011; Kalavrouziotis *et al.* 2015). Regarding biosolids, more than 50% of produced sludge in EU-27 is used in agriculture (Kelessidis & Stasinakis, 2012), more than 40% of biosolids is applied to land in USA and Canada (Citulski & Farahbakhsh, 2010), while the land application of treated sewage sludge is suggested as the optimal solution for efficient sludge management in China (Yang *et al.* 2015).

After treated wastewater and biosolids reuse, the contained micropollutants are subjected to different processes such as runoff to surface water, infiltration to groundwater, biological and abiotic degradation, photodegradation, sorption to suspended solids, colloids and organic matter, volatilization and plant uptake. As a result of these processes, various organic micropollutants as well as their transformation by-products have been detected in river water (Loos *et al.* 2009; Kuzmanovic *et al.* 2015), groundwater (Lapworth *et al.* 2012), seawater (Nödler *et al.* 2016) and soil (Wu *et al.* 2014), worldwide, at concentrations at least one order of magnitude lower that those detected in treated wastewater and biosolids. A brief description of the major mechanisms affecting organic micropollutants' fate is given below.

The great number and diversity of bacteria in the environment often results to significant transformations of the structure and chemical properties of organic micropollutants (Suthersan, 2001). *Biodegradation* of organic micropollutants may occur either as these compounds are used as carbon and energy source from microorganisms or due to co-metabolic phenomena where micropollutants are degraded by enzymes generated for other easily biodegradable substrates. The ability of microorganisms to transform organic micropollutants depends on their ability to produce the appropriate enzymes as well as from the existence of the optimal environmental conditions, the existence of sufficient biomass, the high or low concentration of target compound and their bioavailability (Gavrilescu, 2005). The chemical structure of the organic micropollutants play also important role on their biodegradation. In general, the linear, short side chains compounds, the unsaturated aliphatic compounds, and these with electron donating functional groups are considered as easily degraded substances. On the other hand, the long, highly branched side chains compounds, the polycyclic or saturated compounds, and the compounds possessing halogen, sulphate or electron withdrawing functional groups are considered as persistent micropollutants (Jones *et al.* 2005).

Abiotic degradation may occur due to hydrolysis and oxidation-reduction reactions. During hydrolysis, chemical bonds of micropollutants are broken down due to reaction with water. Typically, some chemical groups of the compounds are replaced by hydroxyl groups. The hydrolysis reactions are affected by system's pH. Several functional groups are susceptible to hydrolysis such as amides, carboxylic acid esters, lactones and phosphoric acid esters; whereas others are not affected by hydrolysis (Neely, 1985). Oxidation-reduction (redox) reactions occur due to the transfer of electrons from the reduced to the oxidized species. Several examples have been observed such as the oxidation of halogenated solvents and the reductive dehalogenation of halogenated compounds.

Photodegradation (photolysis) occurs when the chemical bonds of an organic molecule breakdown due to the application of energy in the form of photons. In *direct photolysis*, direct absorption of photons by the organic molecule occurs, while during *indirect photolysis* photosensitive chemicals found in water such as humic acids and nitrates are excited by absorption of the solar energy, providing photochemical reactions that initiate micropollutants' degradation (Gatidou & Iatrou, 2011). Photodegradation is affected by the system's pH, the available light intensity, the time of exposure, the amount of energy required for breaking of a chemical bond and the existence of the appropriate intermediate compounds (case of *indirect photolysis*) (Gonzalez & Roman, 2005). The existence of suspended solids or/and dissolved organic matter at high concentration result to reduction of organic micropollutant kinetics by clouding sunlight intensity. Photolysis half-lives range between few minutes to several days, depending on the structure of the organic contaminant. During photolysis, several transformation products can be produced.

The *sorption* of micropollutants is affected by system's characteristics (pH, organic matter content, particle distribution, temperature) and the molecular structure, electrical charge and solubility of target micropollutants (Gavrilescu, 2005; Yu *et al.* 2009). Kinetically, the sorption of most organic micropollutants is a two phase process; an initial fast phase which is responsible for the greatest part of the total sorption and a slower one leading to final equilibrium (Pignatello, 1998). It is generally considered that sorbed micropollutants are less accessible to microorganisms and as a result sorption decreases the rate of their degradation (Arias-Estevez *et al.* 2008). However, micropollutants' bioavailability is not only affected by their sorbed amount but also from their distribution among sorption sites of different strengths (Sharer *et al.* 2003).

During *volatilization* micropollutants are distributed to the atmosphere where they can potentially be transferred over long distances. The rate of volatilization is affected by temperature, humidity, air movement and micropollutant properties (vapor pressure, heat of vaporization, partition coefficient between the atmosphere and other phases, solubility) (Gavrilescu, 2005).

Finally, some organic micropollutants tend to *uptake into plants and animals*. The extent of plant uptake depends on micropollutants characteristics, plant species, growth stage and physicochemical soil properties (Gavrilescu, 2005; Eggen & Lillo, 2012).

The role of the aforementioned processes in micropollutants' fate depends on their physico-chemical properties (polarity, water solubility, vapor pressure, sorption potential, persistence) and the type of the environment where the micropollutants are present. Once in the natural environment, hydrophobic organic micropollutants might bind to particles. In fluvial systems, they are transported down-stream with the sediment load, ending up to river banks, lakes, deltas and harbors, while dredging or flooding can result to their remobilization (Gerbersdorf *et al.* 2015). The constantly alternating environmental conditions occurred during transport and deposition of sediments (e.g. changes in pH, oxygen and organic matter concentration) affect the bio- and chemical transformations of non-polar organic micropollutants.

On the other hand, polar organic micropollutants might travel almost unhindered through surface waters and thus it is more likely to reach groundwater resources. Once a micropollutant is found in the soil, it will move through the soil with water, it will attach to soil particles or it will be metabolized by (micro)organisms and free enzymes in the soil. The transport of organic micropollutants in soil column is affected by its texture, permeability, depth, pH and organic matter. High clay content can enhance pollution attenuation due to the very small pore size and the available surface area for cations' sorption. Low soil permeability or/and deeper soils increase the contact time between micropollutants and the soil particles enhancing their sorption. In cases that the degradation rates in soil are much higher comparing to leaching rates, then the micropollutant will not reach the groundwater (Waldman & Shevah, 1993).

12.4 ENVIRONMENTAL THREAT FOR THE AQUATIC AND TERRESTRIAL ENVIRONMENT DUE TO THE OCCURRENCE OF ORGANIC MICROPOLLUTANTS

Several organic micropollutants such as pharmaceuticals and pesticides have been specifically designed to be biologically active; thus, effects on non-target organisms even at trace concentrations are likely to occur. So far, acute toxicity experiments have been conducted for many micropollutants, indicating possible toxic effects for some organic compounds such as pesticides at concentrations similarly to those detected in the environment. Additionally, several studies have shown that the mixtures of some micropollutants such as pharmaceuticals exhibit greater effect than the compounds individually (Petrie *et al.* 2015). A plethora of articles is also available regarding the endocrine disrupting effects of various organic micropollutants such as steroidal estrogens, non-steroidal synthetic estrogenic compounds, PCBs and selected pesticides to the environment (Pojana *et al.* 2004; Matozzo *et al.* 2008). Antibiotic-resistant bacteria and genes have also been found to be transported to the environment through wastewater reuse and biosolids application to the land (Bondarczuk *et al.* 2016). Several organic micropollutants (pesticides, PAHs, surfactants) seem to interfere with organisms' physiology, rendering them less tolerant to the environmental stress caused by extreme levels of natural stressors such as heat stress, freezing temperatures, desiccation, oxygen depletion, starvation and pathogens (Ferreira *et al.* 2008; Holmstrup *et al.* 2010). The bioaccumulation and biomagnification of organic micropollutants in species at the top level of food chain (fish eating birds, marine mammals) has also been reported (Fatta-Kassinos *et al.* 2011). Most of the aforementioned studies have been conducted using aquatic organisms (bacteria, algae, crustaceans, fish), whereas less information is available for the effects of micropollutants on soil organisms.

Limited information is available on the chronic effects of organic micropollutants to the environment (Chalew & Halden, 2009), while more data is needed for their synergistic, antagonistic and additive effects. Benthic organisms can also be exposed to organic micropollutants; however, so far, little relevant toxicological information is available. Additional concerns exist that micropollutants may be taken up by crops plants and enter the food chain (Dolliver *et al.* 2007).

Due to the great number of organic micropollutants that co-exist in the environment; there is a need for prioritization them in order to achieve better monitoring and control (Kumar & Xagoraraki, 2010; von der Ohe *et al.* 2011; Kuzmanovic *et al.* 2015). Under this frame, preliminary risk assessment approaches have been applied in country-level or selected areas to identify the micropollutants posing the higher threat for the aquatic and soil organisms. According to these methodologies, among the most important compounds for the aquatic environment are considered pesticides such as chlorpyriphos, chlorfenvinphos, diazinon, dichlofenthion, prochloraz, ethion carbofuran and diuron (Kuzmanovic *et al.* 2015), as well as emerging contaminants such as nonylphenolic compounds, triclosan and siloxanes (Thomaidi *et al.* 2015; Thomaidi *et al.* 2016).

12.5 REGULATORY FRAMEWORK ON THE OCCURRENCE OF ORGANIC MICROPOLLUTANTS IN TREATED WASTEWATER AND BIOSOLIDS

To date, the legislation on treated wastewater and sludge rarely set discharge guidelines and standards for organic micropollutants. At national level, Switzerland was the first country that decided organic micropollutants' control at the point source, aiming to reduce their loadings by 80% at selected STPs (Bui *et al.* 2016). The indicator compounds selected were benzotriazole, diclofenac, carbamazepine, sulfamethozaxole and mecocrop. In USA, organic micropollutants are not regulated for wastewater discharge; however, some indicator compounds (cotinine, primidone, phenyltoin, carbamazepine, estrone, sucralose, triclosan, atenolol, meprobamate, and diethyltoluamide) have been set for indirect potable reuse (Audenaert *et al.* 2014). Australia has also established threshold values for several organic micropollutants (including pesticides, PAHs, organotins, musks, nonylphenol, triclosan, pharmaceuticals, estrogens) in secondary effluents for reuse in water supplies areas (NRMMC, 2008). In European Union, the Directive 91/271/EU regulating wastewater treatment and discharge (European Economic Community, 1991) does not set values for organic micropollutants, while no Directive exists for wastewater reuse. On the other hand, Greece has set limit values for 40 organic micropollutants (including selected pesticides, VOCs, tributyltin and nonylphenol) in wastewater reuse for agricultural, urban, industrial purposes and aquifer recharge (Joint Ministerial Decision, 2011).

Regarding biosolids, the basic legislative text concerning the sludge reuse in agriculture in European Union is Sewage Sludge Directive 86/278/EEC (European Economic Community, 1986). This text has not set limit values for organic micropollutants. However, nine European countries (Austria, Belgium, Czech Republic, Denmark, France, Germany, Slovenia and Sweden) have included selected organic micropollutants such as PAHs, PCBs halogenated organic compounds, phthalates, and nonylphenols in their national legislations for sludge reuse (Kelessidis & Stasinakis, 2012).

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Index

Wastewater and Biosolids Management

Editor: Ioannis K Kalavrouziotis

Wastewater and Biosolids Management covers a wide range of current, new and emerging topics in wastewater and biosolids. The book addresses the theoretical and practical aspect of the reuse and looks to advance our knowledge on wastewater reuse and its application in agricultural production.

The book aims to present existing modern information about wastewater reuse management based on earlier literature on the one hand and recent research developments, many of which have not so far been implemented into actual practice on the other. It combines the practical and theoretical knowledge about 'wastewater and biosolids management' and in this sense it is useful for researchers, students, academicians as well as for professionals.

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